Chemical & Statistical Thermodynamics

2e

for

CSIR-UGC-NET/JRF|GATE

TIFR | BARC | IISc | DRDO | SLET | NTPC | ONGC-GT | HPCL | Ph.D Entrance

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PREFACE TO THE SECOND EDITION

The book "***Chemical & Statistical Thermodynamics***" is written with the objective of providing description of principles involved in Chemical and Statistical Thermodynamics in Physical Chemistry including their application at a level suitable for post-graduate students of Chemistry in different universities. This book will be highly useful for the candidates preparing for various competitive examinations at national and state levels such as CSIR-UGC-NET, GATE, TIFR, SLET, etc.

In all the competitive examinations such as CSIR-UGC-NET/JRF, GATE, TIFR, SLET, etc. the section of Chemical and Statistical Thermodynamics carry approximately 12-15 percent weightage of total marks.

- In every year CSIR-UGC-NET includes at least 16-20 marks from this section.
- In every year GATE paper includes at least 8-10 marks from this section out of 100 marks.

Apart from NET, GATE and PSUs this book will also be very useful to candidates appearing for various Ph.D entrance examinations.

The book contains a brief description on important topic of Chemical and Statistical Thermodynamics. Students preparing for competitive examinations are advised to go through every topic for their understanding and conceptual clarity and then get into solving the problems.

Much care has been taken to minimize the typographical errors, yet if any noticed, then your suggestions are invited with a view to improve the book in future editions.

We would like to thank our respected faculty members for their valuable inputs in the book. Thanks to Mr. Neeraj Panwar, Mr. Vinay Dwivedi and Mr. Habib Ali for their constructive support in doing corrections and proofreading. A note of thanks also to Mohammad Firoz for formatting, designing and type-setting the book.

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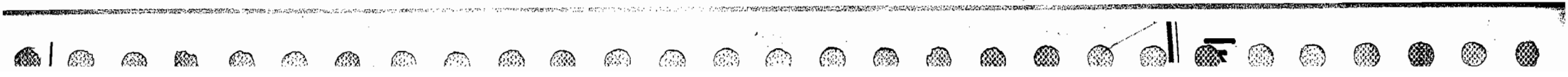


Chapter 1

Introduction to Thermodynamics

Introduction

The subject of thermodynamics deals basically with the interaction of one body with another in terms of the quantities of heat and work. The entire formulation of thermodynamics is based on the two fundamental laws which have been established on the basis of the experimental behaviour of macroscopic aggregates of matter collected over a long period of time. With the help of thermodynamics principles the experimental criteria for equilibrium or for the spontaneity of process are readily established

Mathematics Involved in Chemical Thermodynamics

Differential Formulas:

(i) $\frac{d(c)}{dx} = 0$

(ii) $\frac{d(x^n)}{dx} = nx^{n-1}$

(iii) $\frac{d(cx^n)}{dx} = c\frac{d(x^n)}{dx} = cnx^{(n-1)}$

(iv) $\frac{d(\sin x)}{dx} = \cos x$

(v) $\frac{d(\cos x)}{dx} = -\sin x$

(vi) $\frac{d(a^x)}{dx} = a^x \ln a$

(vii) $\frac{d(e^x)}{dx} = e^x$

(viii) $\frac{d(\ln x)}{dx} = \frac{1}{x},\ x > 0$

(ix) $\frac{d[f(x)g(x)]}{dx} = f(x)\ \frac{d[g(x)]}{dx} + g(x)\ \frac{d[f(x)]}{dx}$

(x) $\frac{d}{dx}\left[\frac{f(x)}{g(x)}\right] = \frac{g(x)\frac{d[f(x)]}{dx} - f(x)\frac{d[g(x)]}{dx}}{[g(x)]^2}$

Integration Formulas:

(i) $\int dx = x + c,\ \int dt = t + c$

(ii) $\int x^n dx = \frac{x^{n+1}}{n+1} + c$

(iii) $\int kx^n dx = k\int x^n dx = k\frac{x^{n+1}}{(n+1)} + c$

(iv) $\int e^x dx = e^x + c$

(v) $\int \frac{1}{x} dx = \ell n_e x + c$

(vi) $\int \sin x\, dx = -\cos x + c$

(vii) $\int \cos dx = \sin x + c$

(viii) $\int [f(x)g(x)]dx = f(x) \int g(x)dx - \int \left[\frac{d}{dx} f(x). \int g(x)dx\right] dx$

Logarithms:

(i) $\log_{10} 2 = 0.3010$ (ii) $\log_{10} 3 = 0.4771$ (iii) $\log_{10} 4 = 0.6020$

(iv) $\log_{10} 5 = 0.699$ (v) $\log_{10} 6 = 0.7781$ (vi) $\log_{10} 7 = 0.8451$

(vii) $\log_{10} 8 = 0.9030$ (viii) $\log_{10} 9 = 0.954$ (ix) $\log_{10} 10 = 1$

Important Rules of Logarithms:

(i) $\ln 2 = 2.303 \times \log_{10} 2 = 2.303 \times 0.3010 = 0.693$

(ii) $\log_{10} x^m = m \log_{10} x$; $\log \frac{m}{n} = \log m - \log n$

(iii) $\log(m \times n) = \log m + \log n$

(iv) $\log_{10} x = -2 \Rightarrow x = 10^{-2} = \frac{1}{100} = 0.01$

(v) $\log_{10}(a/b) = \log_{10} a - \log_{10} b$

(vi) $\log_a e \times \log_e b = \log_a b$

(vii) $\log_{b^n} a^m = \frac{m}{n} \log_b a$

Selected SI units

Quantity	Unit	
Basic Units	**Name**	**Symbol**
Lengths	Metre	m
Mass	Kilogram	kg
Time	Second	s
Electric current	Ampere	A
Temperature	Kelvin	K
Luminous intensity	Candela	cd
Amount of substance	mole	mol
Derived Units:		
Volume	cubic metre	m^3
Density	kilogram per cubic metre	kg/m^2
Force	newton	$N(kg\ m/s^2)$
Pressure	pascal	$Pa(N/m^2)$
Energy, work, heat	joule	J(N-m)

Conversion of Selected Non-system Units to SI units:

Quantity	Unit	Conversion factor to SI
Length	centimetre	1×10^{-2} m
	micrometre(μm)	1×10^{-6} m
	nanometre (nm)	1×10^{-9} m
	angstrom(Å)	1×10^{-10} m
	inch	2.54×10^{-2} m = 2.54 cm
Mass	gram	1×10^{-3} kg
Volume	litre	1×10^{-3} m^3 = 1 dm^3 = 10^3 cm^3
	milli litre	1 cm^3
Pressure	bar	10^5 Pa = 100 kPa
	atmosphere(atm)	1.01325×10^5 Pa = 760 mmHg = 76 cmHg
	millimetre of Hg or torr	133.322 Pa
Energy, work, amount of heat	electron volt(eV)	1.60219×10^{-19} J
	calorie(cal)	4.1868J
	kilocalorie(kcal)	4186.8J
	erg	10^{-7} J

Values of Selected Fundamental Physical Constants

Quantity	Symbol	Value
Planck constant	h	$=6.6262\times10^{-27}$ erg·s
		$=6.6262\times10^{-34}$ J·s(SI)
Avogadro number (Avogadro constant)	N	$=6.022\times10^{23}$ mol^{-1} (SI)
Boltzmann constant	k	$=1.3807\times10^{-16}$ erg deg^{-1} molecule^{-1}
		$=1.3807\times10^{-23}$ JK^{-1} (SI)
Gas constant	R	$=8.314\times10^{7}$ erg deg^{-1} mole^{-1}
		$=8.314$JK^{-1}mol^{-1} (SI)
		$=0.0821$L·atm deg^{-1} mole^{-1}
		$=1.987$cal deg^{-1} mole^{-1}
Molar volume of gas at NTP	V	$=22.414$L mole^{-1}
		$=22.414\times10^{-3}$ m^{3}mole^{-1} (SI)

Velocity of light	c	$= 2.998 \times 10^{10}\ \text{cms}^{-1}$
		$= 2.998 \times 10^{8}\ \text{ms}^{-1}\ (\text{SI})$
Electron mass	m_e	$= 9.109 \times 10^{-28}\ \text{g}$
		$= 9.109 \times 10^{-31}\ \text{kg}\ (\text{SI})$
Electron charge	e	$= 4.803 \times 10^{-10}\ \text{esu}$
		$= 1.602 \times 10^{-19}\ \text{coulomb}\ (\text{SI})$
Faraday constant	F	$= 96485\ \text{coulomb eq}^{-1}$
		$= 96484\ \text{coulomb mol}^{-1}\ (\text{SI})$
Acceleration due to gravity	g	$= 980.665\ \text{cms}^{-2}$
		$= 9.80665\ \text{m s}^{-2}\ (\text{SI})$
Atomic mass unit	amu	$= 1.66 \times 10^{-27}\ \text{kg}\ (\text{SI})$

Function:

Function is a rule that relates two or more variables.

If $z = 3x + y$, where z is a function of x and y. In ideal gas equation P is a function of T and V, T is a function of P and V and V is a function of T and P.

Operator:

An operator is a symbol for a rule for transforming a given mathematical function into another function. It has no physical meaning if written alone. It is represented by cap (^).

Example:

(i) $\frac{d}{dx}$ is an operator which transforms a function into its first derivative with respect to x.

(ii) $\frac{d}{dx}$ transforms the function $\sin x$ into the function $\cos x$.

In general, if $\hat{A}$ denotes an operator which transforms the function $f(x)$ into the function $g(x)$, then we write $\hat{A}f(x) = g(x)$.

Example:

(a) Let $\hat{A}$ be $\frac{d}{dx}$ and $f(x) = ax^2$; then $\hat{A}f(x) = \frac{d}{dx}(ax^2) 2ax$ i.e. $g(x) = 2ax$.

(b) Let $\hat{A}$ be a (i.e. multiplication by a) and $f(x) = x^2 + c$, then $\hat{A}f(x) = a.(x^2 + c) = ax^2 + ac$ i.e. $g(x) = ax^2 + ac$.

Differentiation:

In calculus (a branch of mathematics) the **derivative** is a measure of how a function changes as its input changes. Derivative can be thought of as how much one quantity is changing in response to changes in some other quantity; for example, the derivative of the position of a vehicle with respect to time is the velocity at which the vehicle is traveling. The process of finding a derivative is called **differentiation**. The reverse process is called **antidifferentiation**. The fundamental theorem of calculus states that antidifferentiation is the same as integration.

Differentiation is a method to compute the rate at which a dependent output y changes with respect to the change in the independent input x. This rate of change is called the **derivative** of y with respect to x. The dependence of y upon x means that y is a function of x. This functional relationship is often denoted $y = f(x)$, where f denotes the function. If infinitesimal change in x is denoted by dx, and the derivative of y with respect to x is written as $\frac{dy}{dx}$.

In **mathematics**, a **partial derivative** of a **function** of several variables is its derivative with respect to one of those variables, with the others held constant as opposed to the total derivative.

For a function of several variables, for example f(x,y,z), the partial derivatives are simply usual derivative in one of the variables when you keep the other variables fixed. For example, take

$$f = 3xy + yz^2$$

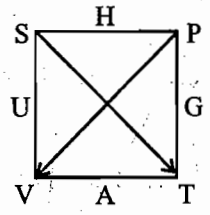
In this example f is a function of x,y and z and we can calculate the value of partial derivative in all form

$$\left(\frac{\partial f}{\partial x}\right)_{y,z}; \left(\frac{\partial f}{\partial y}\right)_{x,z}; \left(\frac{\partial f}{\partial z}\right)_{x,y}$$

Total derivative is just the usual derivative (with respect to x) of the function f. It can be expressed in terms of partial differentiation as

$$df = \left(\frac{\partial f}{\partial x}\right)_{y,z} dx + \left(\frac{\partial f}{\partial y}\right)_{x,z} dy + \left(\frac{\partial f}{\partial z}\right)_{x,y} dz$$

Max-Born thermodynamics Square : Given by German chemist Max-Born with the help of this square we find out nearly all thermodynamics equation related with thermodynamic potential connecting internal energy (U), enthalpy (H), Helmholtz free energy (A) and Gibbs free energy (G), with relevant parameters such as entropy, pressure, temperature and volume, may be put as



$dH = TdS + VdP$ (where, positive sign because S and P at tail of arrow)

Similarly, $dG = VdP - SdT$ (where, negative sign because T at head of arrow)

$dA = -PdV - SdT$ (where, negative sign because V and T at head of arrow)

$dU = TdS - PdV$ (where, negative sign because V at head of arrow)

These equations are known as ***Maxwell equation***.

Maxwell's relationship : From the various expansions

If V is constant so that dV is zero, then,

$$\left(\frac{\partial U}{\partial S}\right)_V = T \qquad \ldots (1)$$

If S constant so that dS is zero,

$$\left(\frac{\partial U}{\partial V}\right)_S = -P \qquad \ldots (2)$$

Differentiating equation (1) with respect to V keeping S constant and differentiationg equation (2) with respect to S keeeping V constant, we get

$$\frac{\partial^2 U}{(\partial S)(\partial V)} = \left(\frac{\partial T}{\partial V}\right)_S \qquad \ldots (3)$$

And

$$\frac{\partial^2 U}{(\partial V)(\partial S)} = \left(\frac{\partial P}{\partial S}\right)_V \qquad \ldots (4)$$

It follows from equation (3) and (4) that

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \qquad \ldots (5)$$

Following the same mathematical procedure as above, the following expressions can be easily derived.

$$\left(\frac{\partial T}{\partial P}\right)_S = -\left(\frac{\partial V}{\partial S}\right)_P \qquad \ldots (6)$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad \ldots (7)$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad \ldots (8)$$

Equation (5) and (8) are known as Maxwell's relationships.

Another set of Maxwell's relationships

$$\left(\frac{\partial U}{\partial S}\right)_V = -\left(\frac{\partial H}{\partial S}\right)_P \quad \ldots (9)$$

$$\left(\frac{\partial U}{\partial V}\right)_S = -\left(\frac{\partial A}{\partial V}\right)_T \quad \ldots (10)$$

$$\left(\frac{\partial H}{\partial P}\right)_S = -\left(\frac{\partial G}{\partial P}\right)_T \quad \ldots (11)$$

$$\left(\frac{\partial A}{\partial T}\right)_V = -\left(\frac{\partial G}{\partial T}\right)_P \quad \ldots (12)$$

PROBLEMS

1. Show that $\left(\frac{\partial U}{\partial S}\right)_P = T - P\left(\frac{\partial T}{\partial P}\right)_S$

Soln. From the combined form of the first and the second laws of thermodynamics, we know that in a system undergoing expansion,

$$dU = TdS - PdV$$

Dividing by dS, keeping P constant, we have

$$\left(\frac{\partial U}{\partial S}\right)_P = T - P\left(\frac{\partial V}{\partial S}\right)_P$$

Since, $\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S$ [From Maxwell's relation]

$\therefore$ $\left(\frac{\partial U}{\partial S}\right)_P = T - P\left(\frac{\partial T}{\partial P}\right)_S$

2. Using the combined form of the first and second law of thermodynamics and appropriate Maxwell relations, derive the two thermodynamics equations of state.

Soln. $dU = TdS - PdV$

Dividing by dV, keeping T constant, we have

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$$

Since, $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ [From Maxwell's relation]

$\therefore$ $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$

This is the first thermodynamic equation of state.

Again, $dH = TdS + VdP$

Dividing by dP, keeping T constant, we have

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V$$

Since, $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$ [From Maxwell's relation]

$\therefore$ $\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$

This is the second thermodynamics equation of state.

3. Indicate which one of the following relations is **NOT** correct. **[NET June 2012]**

(a) $-\left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial P}{\partial S}\right)_V$ (b) $-\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$

(c) $-\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial P}{\partial T}\right)_V$ (d) $-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$

Soln. The correct option is (b)

4. The Maxwell's relationship derived from the equation $dG = VdP - SdT$ is

(a) $\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial S}{\partial P}\right)_T$ (b) $\left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial T}{\partial S}\right)_P$ (c) $\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$ (d) $\left(\frac{\partial P}{\partial V}\right)_T = -\left(\frac{\partial T}{\partial S}\right)_P$

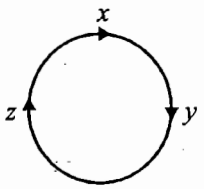
The correct option is (c)

Cyclic Rule :

The **triple product rule**, known variously as the *cyclic chain rule*, *cyclic relation*, or ***Euler's chain rule***, is a formula which relates **partial derivatives** of three interdependent variables. The rule finds application in **thermodynamics**.

The triple product rule for such interrelated variables x, y, and z comes from using a reciprocity relation is given by

$$\boxed{\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1}$$

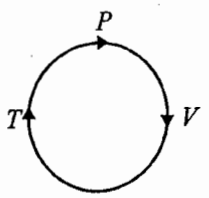


Cyclic Rule in the form of P, V & T:

Let us consider one function and any two variables then we proof that cyclic rule

$P = f(T,V)$, we have

$$dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV$$



Since, P is constant, so $dP = 0$

$$\left(\frac{\partial P}{\partial T}\right)_V (dT)_P + \left(\frac{\partial P}{\partial V}\right)_T (dV)_P = 0$$

dividing by $(\partial V)_P$, we have

$$\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial T}{\partial V}\right)_P+\left(\frac{\partial P}{\partial V}\right)_T=0$$

Or, $$\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial T}{\partial V}\right)_P=-\left(\frac{\partial P}{\partial V}\right)_T$$

Or, $$\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial T}{\partial V}\right)_P\left(\frac{\partial V}{\partial P}\right)_T+1=0$$

Or, $$\boxed{\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial T}{\partial V}\right)_P\left(\frac{\partial V}{\partial P}\right)_T=-1}$$

Thermodynamic Coefficient:

(i) Isobaric thermal expansion coefficient (α):

The degree of expansion divided by the change in temperature at constant pressure is called the material's coefficient of thermal expansion and generally varies with temperature

$$\alpha=\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

(ii) Isothermal Compressibility factor (β):

In thermodynamics and fluid mechanics, **compressibility** is a measure of the relative volume change of a fluid or solid as a response to a pressure (or mean stress) change at constant temperature.

$$\beta=-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

Note: most textbooks use the notation κ for this quantity.

where, V is volume and P is pressure

The above statement is incomplete, because for any object or system the magnitude of the compressibility depends strongly on whether the process is adiabatic or isothermal. Accordingly **isothermal** compressibility is defined as

$$\beta_T=-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

where the subscript T indicates that the partial differential is to be taken at constant temperature

Adiabatic compressibility is defined:

$$\beta_s=-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$$

(iii) Isochoric Thermal Pressure Expansion Coefficeint (γ):

The relative change in pressure with respect changing temperature at constant volume known as isochoric thermal pressure expansion coefficient.

$$\gamma=\frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_V$$

PROBLEMS

1. Using the cyclic rule, show that the thermal coefficients α and β are related as $\alpha = \beta \cdot \gamma P$. Where γ is the pressure coefficient.

Soln. By definition, $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$; $\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ and $\gamma = \frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_V$

Hence, $\left(\frac{\partial V}{\partial T}\right)_P = \alpha V$; $\left(\frac{\partial P}{\partial V}\right)_T = -\frac{1}{\beta V}$ and $\left(\frac{\partial V}{\partial T}\right)_V = \frac{1}{\gamma P}$ ... (i)

From the cyclic rule, $\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial P}{\partial V}\right)_T = -1$ ...(ii)

Substituting equation, **(i) in equation (ii),** we have

$$(\alpha V)\left(\frac{1}{\gamma P}\right)\left(\frac{-1}{\beta V}\right) = -1$$

Or, $\frac{\alpha}{\beta \gamma P} = 1$

Or, $\alpha = \beta \gamma P$

2. Show that for a gaseous substance, $\left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha}{\beta}$

Soln. From the cyclic rule, $\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = -1$

We have, $\left(\frac{\partial P}{\partial T}\right)_V = -\frac{1}{(\partial T/\partial V)_P (\partial V/\partial P)_T} = -\frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T}$

Multiplying the numerator and the denominator on the RHS by 1/V, we obtain

$$\left(\frac{\partial P}{\partial T}\right)_V = -\frac{(1/V)(\partial V/\partial T)_P}{(1/V)(\partial V/\partial P)_T} = \frac{\alpha}{\beta}$$

3. Show that for a gaseous substance, $\left(\frac{\alpha}{\beta}\right) = \frac{R}{(V-b)}$

Soln. We have shown above that $\left(\frac{\alpha}{\beta}\right) = \left(\frac{\partial P}{\partial T}\right)_V$

For a vander waals gas, $\left(P + a/V^2\right)(V-b) = RT$

Or, $P = \frac{RT}{V-b} - \frac{\alpha}{V^2}$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b} = \frac{\alpha}{\beta}$$

Show that $\left(\frac{\partial \alpha}{\partial P}\right)_T = -\left(\frac{\partial \beta}{\partial T}\right)_P$

Soln. Let $V = f(T, P)$

$$dV = \left(\frac{\partial V}{\partial T}\right) dT + \left(\frac{\partial V}{\partial P}\right)_T dP \quad \text{... (i)}$$

Since, by definition, $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$, hence $\left(\frac{\partial V}{\partial T}\right)_P = \alpha V$ ... (ii)

Also, since $\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$, hence $\left(\frac{\partial V}{\partial P}\right)_T = -\beta V$ ... (iii)

Substituting equation (ii) and (iii) in equation (i), we have

$$dV = \alpha V dT - \beta V dP \text{ or } \frac{dV}{V} = \alpha dT - \beta dP$$

Or, $d \ln V = \alpha dT - \beta dP$

Since V is a state function, therefore, using the Euler reciprocal relation, we get

$$\left(\frac{\partial \alpha}{\partial P}\right)_T = -\left(\frac{\partial \beta}{\partial T}\right)_P$$

State Function and Exact differentials :

In thermodynamics, a **state function**, *state quantity*, or a *function of state*, is a property of a system that depends only on the current state of the system, not on the way in which the system acquired that state. For example, internal energy, enthalpy and entropy are *state quantities* .In contrast, mechanical work and heat are process quantities and state functions gives ***exact differentiables***. As E is a state function and dE is an exact differential.

e.g. $dE = \partial q + \partial w$ can be exact differential.

To prove: State function we use Euler's theorem. This theorem applies on linear equation (Not zig-zag equation according to Euler)

If z is function of x and y variable.

$$z = z(x, y)$$

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

Put, $M = \left(\frac{\partial z}{\partial x}\right)_y$, $N = \left(\frac{\partial z}{\partial y}\right)_x$

So, equation change from zig-zag to linear

$dz = Mdx + Ndy$

Than for z being a state function it must follow this relation and dz would be exact differential if

$$\left[\frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right)_y\right]_x = \left[\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial y}\right)_x\right]_y \text{ or } \left(\frac{\partial m}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \text{ is satisfied.}$$

z can be considered as any thermodynamics function E, H, G etc. and x, y may be the thermodynamic variables T, P, V etc. are also state functions.

PROBLEMS

1. Verify whether $dz = xdy + ydx$ is an exact differential or not.

Soln. Here, $M(x,y) = y$ and $N(x,y) = x$

Hence, $\left(\frac{\partial M}{\partial y}\right)_x = 1$ and $\left(\frac{\partial N}{\partial x}\right)_y = 1$

Thus, $\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$

Hence, dz is an exact differential.

2. The exact differential df of a state function $f(x,y)$ among the following is **[NET Dec. 2014]**

(a) xdy (b) $dx - \frac{x}{y}dy$ (c) $ydx - xdy$ (d) $\frac{1}{y}dx - \frac{x}{y^2}dy$

Soln. If $df = \frac{1}{y}dx - \frac{x}{y^2}dy$

Here, $M(x,y) = \frac{1}{y}$ and $N(x,y) = -\frac{x}{y^2}$

Hence, $\left(\frac{\partial M}{\partial y}\right)_x = -\frac{1}{y^2}$ and $\left(\frac{\partial N}{\partial x}\right)_y = -\frac{1}{y^2}$

Thus, $\left(\frac{\partial N}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$

Hence, df is an exact differential.

Essential Criteria of a state function :

The essential criteria of a state function are as follows :

- The change in the value of a state function depends only the initial and final states and not on the path of the process carried out in going from initial state to final state.
- The cyclic integration involving a state function is zero
- The state function has an exact differential, i.e. if $P = f(T,V)$ is a state function then

$$dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV$$

with the condition that

$$\frac{\partial}{\partial V}\left\{\left(\frac{\partial P}{\partial T}\right)_V\right\}_T = \frac{\partial}{\partial T}\left\{\left(\frac{\partial P}{\partial V}\right)_T\right\}_V$$

- All thermodynamics properties satisfy the requirements of state function. A few of them are

$\Delta U = q + w$ change in thermodynamics energy

$S = \frac{q_{rev}}{T}$ entropy

$H = U + PV$ enthalpy

$G = H - TS$ Gibb's free energy

$A = U - TS$ Helmohltz free energy

$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j,j\neq i}$ chemical potential.

PROBLEMS

1. Verify whether $dz = \left(51x^2y + 47y^4\right)dx + \left(17x^3 + 188xy^3\right)dy$ is an exact differential or not.

Soln. Here, $M(x,y) = 51x^2y + 47y^4$ and $N(x,y) = 17x^3 + 188xy^3$

Hence, $\left(\frac{\partial M}{\partial y}\right)_x = 51x^2 + 188y^3$ and $\left(\frac{\partial N}{\partial x}\right)_y = 51x^2 + 188y^3$

Thus, $\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$

Hence, dz is an exact differential.

2. Writing V as a function of T and P, show that for an ideal gas, dV is an exact differential.

Soln. $V = f(T,P)$

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \quad \text{... (i)}$$

For an ideal gas, $PV = RT$ so that $V = RT/P$. Hence,

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} \text{ and } \left(\frac{\partial V}{\partial P}\right)_T = \frac{R}{P} \text{ and } \left(\frac{\partial V}{\partial P}\right)_T = -\frac{RT}{P^2} \quad \text{... (ii)}$$

Substituting equation (ii) in equation (i), we get

$$dV = \left(\frac{R}{P}\right)dT - \left(\frac{RT}{P^2}\right)dP$$

According to the Euler reciprocal relation, dV would be an exact differential if

$$\left[\frac{\partial(R/P)}{\partial P}\right]_T = -\left[\frac{\partial(RT/P^2)}{\partial T}\right]_P$$

Or, if $-\frac{R}{P^2} = -\frac{R}{P^2}$ which is true.

System and Surroundings

A system is that part of universe which is under thermodynamic study and the rest of universe is called surroundings. A system is made up of one or more than one phase and is called homogenous and heterogenous systems respectively.

A phase is defined as homogenous, physically distinct and mechanically seperable portion of system.

Types of system:

Depending upon nature of boundary between system and surroundings:

(a) ***Isolated system*:** If the boundary prevents any interaction with the surroundings, the system is called isolated system.

OR

A system is said to be isolated when it can neither exchange energy nor matter with its surroundings.

e.g. – Boiling water, A cup of tea in thermus flask.

(b) ***Open system*:** If the matter and energy both can pass across the boundary, the system is called open system.

e.g. – Tea kept in cup.

(c) ***Closed system*:** If matter can't exchange but energy exchange it is called closed system.

e.g. – Tea kept in kettle.

Extensive Property or variable: That properties which depend on mass or size are known as extensive property. e.g. volume, energy, heat capacity enthalpy, entropy, free energy, length, mass etc.

Intensive Property or variable : That properties which does not depend on mass or size are knonw as intensive property e.g. temperature, pressure, concentration, density, dipole moment, viscosity, surface tension, molar volume, dielectric constant, colour etc.

Thermodynamic process:

It is the path or operation by which a system changes from one state to another.

1. **Isothermal process:** Temperature of system remains constant during each step.

$T = \text{constant.} \quad \Rightarrow \quad dT = 0$

Details:

(i) For such change system should be contained in a perfectly coducting container.

(ii) Perfect isothermal change is impossible but when a change is carried out very slowly approximate isothermal change occurs.

(iii) It follows Boyle's law.

(iv) Work done in isothermal process is graphically given by area under P-V curve.

(v) $\Delta H = nC_P.\Delta T$ and $\Delta E = nC_V.\Delta T$

In isothermal process $\Delta T = 0$

$\therefore \quad \Delta H = 0$ and $\Delta E = 0$

(vi) Specific heat at constant T is infinitely great in isothermal process.

2. **Adiabatic process:** There is no heat exchange between system and surroundings.

$q = \text{constant.}$

$dq = 0$

Perfectly adiabatic change is impossible but when a process is carried out very rapidly fairly approximate adiabatic change occurs.

3. **Isobaric process:** It is the process in which pressure of the system remains constant during each step.

$P = \text{constant}$

$dP = 0$

4. **Polytropic process:** In this process heat capacity of the body remains constant.

$C_P = \text{constant}$ and $C_V = \text{constant}$

$dC_P = 0$ and $dC_V = 0$

5. **Quasistatic process:** The processs in which the deviation from thermodynamic equilibrium is infinitesimal and all the states through which the system passes can be considered as equilibrium states.

6. **Isochoric process:** When these is no change in the volume of the system during various operations the change is said to be isochoric.

$V = \text{constant.}$

$\Rightarrow \quad dV = 0$

The combustion of a substance in a bomb calorimeter is isochoric process.

7. **Cyclic process:** The process which brings back a system to its original state after a series of changes is called a cyclic process.

As the E and H depends only on their state.

$\therefore$ E and H are constant

So, $dE = 0$ and $dH = 0$

Reversible process: A thermodynamically reversible process is one in which all changes occuring in any part of the process are exactly reversed when it is carried out in opposite direction.

***Characteristics of reversible process*:**

1. It has to be carried out in infinitesimal amounts and hence require infinite time. Therefore changes in this process are very slow.
2. At all time, during the process, the driving force for the change is opposed by a restraining force infinitesimally smaller than the driving force.
3. It can be reversed by infinitesimal increase in opposing force.
4. The work produced in a reversible process is maximum.

Irreversible process: The process which occurs suddenly or spontaneously without the restriction of occuring in successive stages of infinitesimal quantities.

For such process driving force is very much greater than opposing force; so these can't be reversed. These are also called spontaneous process.

***Characteristics of irreversible process*:**

1. If the changes be reversed, the work in the forward direction and in the backward process would be unequal.
2. If initial and final stages be specified, the internal energy change would always be same, whether the process has been affected reversibly or irreversibly.
3. In an irreversible process, since work terms (dw) in two opposite directions are unequal, the heat transfers (dq) would also be unequal.
4. All natural processes are irreversible.

e.g. $\Rightarrow$ (i) flow of heat from high temperature to low temperature;
(ii) Exapansion of gas from higher pressure to lower pressure.

Internal Energy:

Inernal energy is the energy associated with a system by virtue of its molecular consitution and motion of its molecules.

It depends upon internal potential energy and internal kinetic energy.

E_{Total} = Internal potential + Internal kinetic enegy

$$\boxed{E_{Total} = E_t + E_r + E_v + E_b + E_e + E_0 + V_T + E_{nuc}}$$

where E_t = Translational K.E. E_e = Electronic energy
E_r = Rotational K.E. E_0 = Zero point energy
E_V = Vibrational K.E. E_{nuc} = Energy due to interaction between nuclei.
E_b = Bond energy V_T = Intermolecular interaction energy.

$\Rightarrow$ It is an extensive property (E and ΔE both).

$\Rightarrow$ Internal energy is a state function.

$$dE = E_2 - E_1 = E_{final} - E_{initial}$$

It follows Euler's theorem of Exactness.

Sign of ΔE:

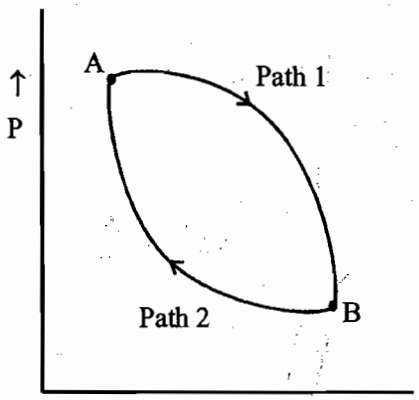
1. If $E_1 > E_2$ $\therefore$ $\Delta E = -ve$

i.e. energy will be absorbed by the sytem from its surroundings.

Hence reaction will be exothermic.

$\Rightarrow$ For cyclic process

$$\sum \Delta E = 0 \; ; \; \oint dE = 0$$



Work:

Any quantity that flows across the boundary of a system during a change in its state and is completely convertible into the lifting of a weight in the surroundings.

1. Pressure - Volume work or work of expansion of gas:

$$W = -\left[\left(F_{ext} \times \text{distance through which piston moves } (\Delta\ell)\right)\right] = -\left[F_{ext} \times \text{Area} \times (\Delta\ell)\right]$$

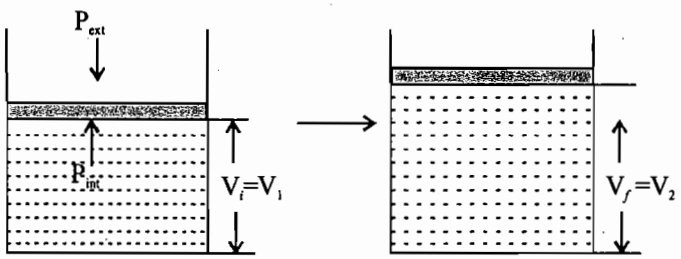
$$\boxed{W = -P_{ext}.\Delta V} \qquad [\because \text{Area} \times \Delta\ell = \Delta V]$$

Or $\boxed{W = -P_{ext}(V_2 - V_1)}$

(a) for expansion $V_2 > V_1$, thus W = negative

(b) for compression $V_1 > V_2$, thus W = positive

2. Isothermal reversible expansion work of ideal gas



Expansion will take place only when

$P_{int} > P_{ext}$

Where, P_{int} = Pressure exerted by gas (Internal pressure)

P_{ext} = External pressure or atmospheric pressure

Work done, $W = -\int dW = -\int_{V_1}^{V_2} P dV$

$$W = -\int_{V_1}^{V_2} P dV \quad (w = -PdV) \qquad \ldots(1)$$

For an ideal gas, we know that

$PV = nRT$

$$P = \frac{nRT}{V}$$

Putting this value of P in equation (1), we get

$$W = \int_{V_1}^{V_2} \frac{nRT}{V} dV \Rightarrow W = -nRT \int_{V_1}^{V_2} \frac{dV}{V} \Rightarrow W = -nRT\,[\ln V]_{V_1}^{V_2} = -nRT \ln\left(\frac{V_2}{V_1}\right)$$

$$\boxed{W=-2.303nRT\log_{10}\left(\frac{V_2}{V_1}\right)}$$

Since $V_2 > V_1$ (due to expansion)

$$\Rightarrow \quad \frac{V_2}{V_1} > 1 \Rightarrow \log_{10}\left(\frac{V_2}{V_1}\right) > 1;\ W < 0$$

i.e $W_{isothemal} < 0$

i.e. Work is done by the system.

3. Isothermal irreversible expansion work of an ideal gas

(i) Free expansion (in vacuum):

When an ideal gas is expanded isothermally in vacuum from a volume V_1 to V_2 irreversibly, Then

Work done $= -P_{ext}(V_2 - V_1) = 0$

Since in vacuum there is no external pressure on the gas

(ii) When the ideal gas is expanded isothermally from a volume V_1 to V_2 irreversible upto a constant external pressure P_{ext} and if $P_{ext} < P_{gas}$, then

$$\boxed{\text{Work done} = -P_{ext}(V_2 - V_1)}$$

4. Reversible adiabatic expansion of an ideal gas:

Starting with the proof of $TV^{\gamma-1} = \text{constant}$ **[Geo-chemist exam 2015]**

Proof : From the 1st law of thermodynamics, we know that,

$dQ = dU + dW$ ... (1)

But for an adiabatic process, Q is constant i.e $dQ = 0$

$0 = dU + dW$

$dU + dW = 0$

$dU + dW = 0$

Sine, $dU = nC_V dT$ and $dW = PdV$

$\Rightarrow \quad nC_V dT + PdV = 0$ ... (2)

For one mol $n = 1$

$\Rightarrow \quad C_V dT + PdV = 0$

$\Rightarrow \quad C_V dT + PdV = 0$ ... (3)

Now for one mole of an ideal gas, we know that

$$PV = RT \Rightarrow \quad P = \frac{RT}{V}$$

Now putting this value of P in equation (3), we get

$$C_V dT + \left(\frac{RT}{V}\right) dV = 0 \quad \Rightarrow C_V \frac{dT}{T} + R\frac{dV}{V} = 0$$

$$\Rightarrow \quad C_V \frac{dT}{T} + (C_P - C_V)\frac{dV}{V} = 0 \quad [\because R = C_P - C_V]$$

$$\Rightarrow \quad \frac{dT}{T} + \left(\frac{C_P}{C_V} - 1\right)\frac{dV}{V} = 0 \Rightarrow \frac{dT}{T} + (\gamma - 1)\frac{dV}{V} = 0$$

Integrating both sides, we get,

$$\int \frac{dT}{T} + (\gamma - 1)\int \frac{dV}{V} = 0$$

$\Rightarrow \quad \ln T + (\gamma - 1)\ln V = \ln C \Rightarrow \ln T + \ln V^{(\gamma-1)} = \ln C$

$\Rightarrow \quad \ln TV^{(\gamma-1)} = \ln C$

Taking antilog, we get $TV^{(\gamma-1)} = C$

i.e. $\boxed{TV^{(\gamma-1)} = \text{constant}}$ ... (4)

Now, for 1 mol of an ideal gas, we know that,

$PV = RT \Rightarrow T = \frac{PV}{R}$

Putting this value of T in (4), we get

$\left(\frac{PV}{R}\right)V^{(\gamma-1)} = \text{constant}$

[$\because$ R is also a constant]

$\Rightarrow \quad \boxed{PV^{\gamma} = \text{constant}}$ ... (5)

Again, for one mol of an ideal gas, we have

$PV = RT \qquad \Rightarrow V = \frac{RT}{P}$

Now putting this value of V in equation (4). we get

$T\left(\frac{RT}{P}\right)^{\gamma-1} = \text{constant}$

$\boxed{T^{\gamma}P^{(1-\gamma)} = \text{constant}}$

Problem. A given mass of a gas at 0°C is compressed reversiblly and adiabatically to a pressure 20 times the initial value what is the final temp of the gas. [Given : $\gamma = 1.42$]

(a) 66.21 K (b) 77.21 K (c) 60.21 K (d) 70.21 K

Soln. We know that,

$T^{\gamma} P^{(1-\gamma)} = \text{Constant}$

$\Rightarrow \quad T_1^{\gamma} P_1^{(1-\gamma)} = T_2^{\gamma} P_2^{(1-\gamma)}$

$\Rightarrow \quad \left(\frac{T_1}{T_2}\right)^{\gamma} = \left(\frac{P_2}{P_1}\right)^{(1-\gamma)}$ ... (1)

Here,

$T_1 = 0°C = 273\ K,\ T_2 = ?,\ P_1 = P_1,\ P_2 = 20P_1\ \&\ \gamma = 1.42$

Putting all there values in Equation (1), we get

$\left(\frac{273}{T_2}\right)^{1.42} = \left(\frac{20P_1}{P_1}\right)^{1-1.42} \Rightarrow \left(\frac{273}{T_2}\right)^{1.42} = (20)^{-0.4.2}$

Taking log, we get, $1.42 \log_{10}\left(\frac{273}{T_2}\right) = -0.42 \log_{10}(20)$

$\Rightarrow \quad 1.42 \log_{10}(273) - 1.42 \log_{10} T_2 = -0.42 \log_{10}(2\times 10)$

$\Rightarrow \quad 1.42 \log_{10} T_2 = 1.42 \log_{10} 273 + 0.42 \left[\log_{10} 2 + \log_{10} 10\right]$

$\Rightarrow \quad \log_{10} T_2 = 4.00577/1.42 = 2.820$

Taking antilog, we get

$T_2 = 10^{2.820} = 66.21$ K

Correct option is (a)

5. Work done in reversible adiabatic expansion for an ideal gas:

$$\int dw = -\int_{V_1}^{V_2} P dV \quad \ldots (i)$$

$$\Rightarrow \quad w = -\int_{V_1}^{V_2} P dV \quad \ldots (ii)$$

Now we know that for adiabatic process, $PV^{\gamma} = \text{constant}$

$$\Rightarrow \quad PV^{\gamma} = K \quad \Rightarrow P = KV^{-\gamma}$$

Also $P_1V_1^{\gamma} = P_2V_2^{\gamma} = K \quad \ldots (iii)$

Now putting this value of P in equation (ii), we get

$$w = -\int_{V_1}^{V_2} KV^{-\gamma} dV \Rightarrow w = -K\int_{V_1}^{V_2} V^{-\gamma} dV \Rightarrow w = -K\left[\frac{V^{-\gamma+1}}{-\gamma+1}\right]_{V_1}^{V_2}$$

$$\Rightarrow \quad w = \frac{-K}{1-\gamma}\left[V_2^{1-\gamma} - V_1^{1-\gamma}\right]$$

$$\Rightarrow \quad w = \frac{-1}{(1-\gamma)}\left[KV_2^{1-\gamma} - KV_1^{1-\gamma}\right]$$

$$\Rightarrow \quad w = \frac{1}{(\gamma-1)}\left[P_2V_2^{\gamma}V_2^{1-\gamma} - P_1V_1^{\gamma}V_1^{1-\gamma}\right] \quad \text{[Using (iii)]}$$

$$\Rightarrow \quad \boxed{w = \frac{1}{(\gamma-1)}(P_2V_2 - P_1V_1)} \quad \ldots (iv)$$

Now for an ideal gas, we know that, $PV = nRT$

$\Rightarrow \quad P_1V_1 = nRT_1 \quad \ldots (v)$

And $P_2V_2 = nRT_2 \quad \ldots (vi)$

Equation, (vi) – (v), we get

$\Rightarrow \quad P_2V_2 - P_1V_2 = nR(T_2 - T_1)$

Now making this substitution in equation (iv), we get

$$\boxed{w = \frac{1}{(\gamma-1)}nR(T_2 - T_1)}$$

6. Work done in irreversible adiabatic expansion for an ideal gas:

(i) Free expansion (in vacuum):

When an ideal gas is expanded adiabatically (in vacuum) from a volume V_1 to V_2 irreversibly, Then

$$\text{work done} = -P_{ext}(V_2 - V_1) = 0$$

Since in vacuum there is no external pressure on the gas

(ii) When the ideal gas is expanded adiabatically from a volume V_1 to V_2 irreversibly upto a constant external pressure P_{ext} and if $P_{ext} < P_{gas}$, Then

Work done $= -P_{ext}(V_2 - V_1) \quad \ldots (i)$

Now from the 1st low of thermodynamics, we know that

$dQ = dU + dW$

$0 = dU + dW$ [$\therefore$ For adiabatic Process Q = constant]

$\Rightarrow \quad 0 = nC_V dT + PdV \Rightarrow 0 = nC_V(T_2 - T_1) + P(V_2 - V_1)$

$\Rightarrow \quad -P(V_2 - V_1) = nC_V(T_2 - T_1) \Rightarrow (V_2 - V_1) = -\frac{nC_V}{P}(T_2 - T_1)$

Now making this substitution in equation (i), we get

$\Rightarrow$ $\boxed{\text{Work done}(w) = nC_V \frac{P_{ext}}{P}(T_2 - T_1)}$ [Where, P is pressure of the gas]

(iii) We know that, work done in reversible adiabatic expansion (w) is given as:

$$w = \frac{nR}{(\gamma - 1)}(T_2 - T_1) = \frac{nR}{\left(\frac{C_P}{C_V} - 1\right)}(T_2 - T_1) = \frac{n(C_P - C_V)}{\left(\frac{C_P - C_V}{C_V}\right)}(T_2 - T_1) = \frac{nC_V R}{R}(T_2 - T_1) = nC_V dT$$

Since, W = dU (Change in internal energy)

So, $\boxed{dU = nC_V dT}$

i.e. in reversible adiabatic expansion, the work done is equal to the change in internal energy.

PROBLEMS

1. Prove that from cycle rule for $PV_m = RT$

Soln. Differentiating the given equation, $PV_m = RT$, we have

$$PdV_m + V_m dP = RdT$$

Dividing the equation by dT and introducing the condition of constant volume, we get

$$PdV_m + V_m dP = RdT$$

Dividing the equation by dT and introducing the condition of constant volume, we get

$$V_m\left(\frac{\partial P}{\partial T}\right)_{V_m} = R \text{ i.e. } \left(\frac{\partial P}{\partial T}\right)_{V_m} = \frac{R}{V_m}$$

Similarly, we have

$$\left(\frac{\partial T}{\partial V_m}\right)_P = \frac{P}{R} \text{ and } \left(\frac{\partial V_m}{\partial P}\right)_T = -\frac{V_m}{P}$$

Now substituting these in the cyclic rule of $\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial T}{\partial V}\right)_P\left(\frac{\partial V}{\partial P}\right)_T + 1 = 0$, we get

$$\left(\frac{\partial P}{\partial T}\right)_{V_m}\left(\frac{\partial T}{\partial V_m}\right)_P\left(\frac{\partial V_m}{\partial P}\right)_T + 1 = \left(\frac{R}{V_m}\right)\left(\frac{P}{R}\right)\left(-\frac{V_m}{P}\right) + 1 = -1 + 1 = 0$$

2. Test the cyclic rule for

$$\left(P + \frac{a}{V_m^2}\right)(V_m) = RT$$

Soln. From given equation, $\left(PV_m + \frac{a}{V_m}\right) = RT$ and then differentiating, we have

$$PdV_m + V_m dP - \frac{a}{V_m^2} dV_m = RdT$$

Dividing by dT introducing the condition of constant volume, i.e. $dV_m = 0$, we get

$$V_m \left(\frac{\partial P}{\partial T}\right)_V = R \text{ i.e. } \left(\frac{\partial P}{\partial T}\right)_{V_m} = RdT$$

Similarly, we have

$$\left(\frac{\partial T}{\partial V_m}\right)_P = \frac{P - a/V_m^2}{R} \text{ and } \left(\frac{\partial V_m}{\partial P}\right)_T = -\frac{V_m}{P - a/V_m^2}$$

Substituting these in the cyclic rule, we get

$$\left(\frac{\partial P}{\partial T}\right)_{V_m}\left(\frac{\partial T}{\partial V_m}\right)_P\left(\frac{\partial V_m}{\partial P}\right)_T + 1 = \left(\frac{R}{V_m}\right)\left(\frac{P - a/V_m^2}{R}\right)\left(-\frac{V_m}{P - a/V_m^2}\right) + 1 = -1 + 1 = 0$$

3. Show that the pressure is a state function for a gas obeying

$$\left(P + \frac{a}{V_m^2}\right)(V_m) = RT$$

Soln. Given that, $P = \frac{RT}{V_m} - \frac{a}{V_m^2}$

Therefore, $\left(\frac{\partial P}{\partial V_m}\right)_T = -\frac{RT}{V_m^2} + \frac{2a}{V_m^3}; \quad \left(\frac{\partial P}{\partial T}\right)_{V_m} = \frac{R}{V_m}$

$$\frac{\partial^2 P}{\partial T\, \partial V_m} = -\frac{R}{V_m^2} \text{ and } \frac{\partial^2 P}{\partial V_m \partial T} = -\frac{R}{V_m^2}$$

Hence, $\frac{\partial^2 P}{\partial T \partial V_m} = \frac{\partial^2 P}{\partial V_m \partial T}$.

Therefore, dP is an exact differential and P is a state function.

4. From the following thermodynamics relation,

$$G = H - TS;\ H = U + PV;\ dq_{rev} = TdS;\ dU = dq_{rev} - PdV$$

Show that, $\left(\frac{\partial G}{\partial T}\right)_P = -S;\ \left(\frac{\partial G}{\partial P}\right)_T = V$ and $\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$

Soln. We start with,

$$G = H - TS$$

Since, $H = U + PV$

Therefore, $G = U + PV - TS$

Differential of this expression is,

$$dG = dU + PdV + VdP - TdS - SdT$$

Now, $TdS = dq_{rev} = dU + PdV$,

Therefore, $dG = VdP - SdT$ ... (i)

Thus, we establish that G is a function of T and P. Moreover since G is a state function, therefore, we have

$$dG = \left(\frac{\partial G}{\partial P}\right)_T dP + \left(\frac{\partial G}{\partial T}\right)_P dT \quad \text{... (ii)}$$

Comparing equation (i) and (ii), we get

$$\left(\frac{\partial G}{\partial P}\right)_T = V \text{ and } \left(\frac{\partial G}{\partial T}\right)_P = -S$$

Applying Euler's reciprocity relation to equation (i), we get

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

5. Considering U as a function of any two of the variables P, V and T, prove that

(i) $\left(\frac{\partial U}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -\left(\frac{\partial U}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T$ (ii) $\left(\frac{\partial U}{\partial P}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T$

Soln. (i) Given that, $U = f(T, P)$ we get

$$dU = \left(\frac{\partial U}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial P}\right)_T dP$$

Dividing by dP and introducing the conditiion of constant V, we have

$$\left(\frac{\partial U}{\partial P}\right)_V = \left(\frac{\partial U}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V + \left(\frac{\partial U}{\partial P}\right)_T$$

Or, $\left(\frac{\partial U}{\partial P}\right)_V - \left(\frac{\partial U}{\partial P}\right)_T = \left(\frac{\partial U}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V$ ... (i)

Now, $U = f(P, V)$, we get

$$dU = \left(\frac{\partial U}{\partial P}\right)_V dP + \left(\frac{\partial U}{\partial V}\right)_P dV$$

Divindg by dP and introducing the condition of constant T, we have

$$\left(\frac{\partial U}{\partial P}\right)_T = \left(\frac{\partial U}{\partial P}\right)_V + \left(\frac{\partial U}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T$$

Or, $\left(\frac{\partial U}{\partial P}\right)_T - \left(\frac{\partial U}{\partial P}\right)_V = \left(\frac{\partial U}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T$ ... (ii)

Comparing equation (i) and (ii), we have the required relation,

$$\left(\frac{\partial U}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -\left(\frac{\partial U}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T$$

(ii) Since $U = f(T, V)$, we get

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

Diving by dP and introducing the condition of constant temperature $(dT = 0)$, we have

$$\left(\frac{\partial U}{\partial P}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T$$

6. Two moles of a monoatomic gas expand adiabatically in a reversible manner on heating 27°C to 327°C. Then calculate total change in internal energy of the entire process.

Soln: We know that, chnage in internal energy (dU) is given as

$dU = nC_V dT$

$\Rightarrow$ $dU = nC_V (T_2 - T_1)$ ... (i)

Here, dU = change in internal energy and n = 2 moles

For monoatomic gas, $C_V = \frac{3}{2} R$

Given, $T_1 = 27°C = (27 + 273)\ K = 300\ K$

$T_2 = 327°C = (327 + 273)\ K = 600\ K$

Now putting all these values in equation (i), we get change in internal energy

$$\Rightarrow \quad dU = 2\text{mol} \times \frac{3}{2} \times R(600 - 300)\ K = 3 \times 2 \times \frac{\text{cal}}{\text{k.mol}} \times 300\ \text{mol K}$$

$\Rightarrow$ $dU = 1800$ cal

7. The temperature of 54g of water is raised from 15°C to 75°C at constant pressure. The change in the enthalpy of the system (given that $C_{p.m}$ of water = 75 $JK^{-1}mol^{-1}$) is **[GATE 2007]**

(a) 4.5 kJ (b) 13.5 kJ (b) 9.0 kJ (d) 18.0 kJ

Soln. Since, we know that,

$dH = nCpdT$

$$\text{Since number of mole (n)} = \frac{\text{wt. in gm}}{\text{molecular wt.} \times \frac{\text{gm}}{\text{mole}}}$$

$$n = \frac{54}{18} = 3\ mole$$

And $T_1 = 273 + 15 = 288K$ and $T_2 = 23 + 75 = 348K$

$$dT = T_2 - T_1 = 348 - 288 = 60K$$

$$dH = 3 \times 75 JK^{-1} mol^{-1} \times 60\dot{K} = 13500J = 13.5kJ$$

Correct option is (b)

PRACTICE SET

1. What is a cyclic rule ? Derive this rule for a function $Z = f(x, y)$

2. Show that the volume of the following equations is a state function :
(i) Ideal gas equation

(ii) Real gas at low pressure for which van der waals equation reduces to $\left(P + \frac{n^2 a}{V^2}\right)(V) = nRT$

3. An arbitrary variable ϕ is found to have the following relationship

$$d\phi = \frac{RT}{P} dP - RdT$$

Are the following statements correct? Justify your answers
(a) ϕ is a state function
(b) $d\phi$ is an exact differential.
(c) $\oint d\phi \neq 0$
(d) It is possible to wrie down ϕ explicitly in terms of T and P as the independent variables, i.e. $\phi = f(T, P)$.

4. From cyclic rule,

show that , $\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$ **[GATE 1991]**

5. For an ideal gas **[GATE 2010]**

(a) $\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = 0$ (b) $\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = -1$

(c) $\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = +1$ (d) $\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = +2$

6. Among W (work), Q (heat), U(internal energy) and S(entropy) **[GATE 2010]**
(a) W and U are path functions but Q and S are state functions.
(b) W and S are path functions but Q and U are state functions.
(c) S and U are path functions but Q and W are state functions.
(d) W and Q are path functions but U and S are state functions.

7. Match the following: **[GATE 2004]**

P. $\left(\frac{\partial U}{\partial S}\right)_V$	I. A
Q. $\left(\frac{\partial U}{\partial V}\right)_S$	II. –S
R. $\left(\frac{\partial G}{\partial P}\right)_T$	III. T
S. $\left(\frac{\partial G}{\partial T}\right)_P$	IV. –P

V. H
VI. V

(a) P-III Q-IV R-VI S-II (b) P-III Q-I R-II S-V
(c) P-I Q-III R-V S-II (d) P-IV Q-III R-VI S-V

8. Indicate which one of the following relations is **NOT** correct. **[NET June 2012]**

(a) $-\left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial P}{\partial S}\right)_V$ (b) $-\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$

(c) $-\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial P}{\partial T}\right)_V$ (d) $-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$

9. From the following thermodynamic relations

$A = U - TS; \quad dq = TdS; \quad dU = dq - pdV$

Show that

(i) $\left(\frac{\partial A}{\partial V}\right)_T = -P$ (ii) $\left(\frac{\partial A}{\partial T}\right)_V = -S$ (iii) $\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$

10. The Maxwell's relationship derived from the equation $dG = VdP - SdT$ is **[NET Dec. 2013]**

(a) $\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial S}{\partial P}\right)_T$ (b) $\left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial T}{\partial S}\right)_P$ (c) $\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$ (d) $\left(\frac{\partial P}{\partial V}\right)_T = -\left(\frac{\partial T}{\partial S}\right)_P$

ANSWER KEY					
Questions	5	6	7	8	10
Option	(b)	(d)	(b)	(b)	(c)

Chapter 2

Zeroth & First law of Thermodynamics

Introduction

The Zeroth Law of Thermodynamics also known as the law thermal equilibrium was put forward much afte the establishment of the first and second laws of thermodynamics.

Two systems in thermal equilibrium with a third system are also in thermal equilibrium with each other.

Zeroth Law of Thermodynamics:

If body A is in equilibrium with body C and body B is also in equilibrium with body C, then bodies A and B ar in equilibrium with each other. In other words, if systems A and B are placed in contact with each other, n exchange of heat will take place. Recording of temperature of a system by a thermometer is also based on thi law. When a thermometer is placed in the system, it comes to thermal equilibrium with the latter and thu records a constant value.

First law of thermodynamics:

It is the law of conversation of energy and can be stated in various ways.

(i) "The total mass and energy of an isolated system remains constant"

(ii) "Energy can be transformed from one form to another form but energy can neither be created nor destroyed."

(iii) It is impossible to construct a perpetual motion machines which could produce work without consumin any energy."

Mathematically, $\boxed{dU = dq + dw}$

$$\text{State A} \longrightarrow \text{State B}$$

$$\Rightarrow \quad \int_A^B dU = \int_A^B dq + \int_A^B dw \quad \Rightarrow U_B - U_A = q + w$$

Or $\boxed{\Delta U = q + w}$ ... (1)

It may be noted that the values of both q and w depend upon the path followed in going from state A to stat B, but the algebraic sum of these two quantities is independent of the path. Thus (q + w) is state function.

At constant volume

$$dV = 0$$

$$W = -P_{ex}\, dV = 0$$

$\therefore$ from equation (1)

$$\boxed{\Delta U = q_v}$$

Thus heat absorbed at constant volume increases the internal energy.

At constant temperature

$$\Delta U = 0$$

$$\therefore \quad q + w = 0 \quad \Rightarrow q = -w$$

Thus amount of heat absorbed by the system from the surroundings is equal to the work done by the system on the surroundings.

$\Rightarrow$ For cyclic process

$$\Delta U = 0$$

$\therefore$ $q + w = 0$

$\Rightarrow$ At constant pressure

$q_p = H$ = enthalpy

$\therefore$ first law becomes

$$\Delta U = H + W$$

$\Rightarrow$ For adiabatic process

$q = 0$

$\therefore$ $\Delta U = 0 + W \Rightarrow \Delta U = W \Rightarrow \Delta U = -P_{ext}(\Delta V)$

Thus work is equal to the loss in internal energy.

Enthalpy or heat content (H):

Thermal changes occuring at constant pressure is called as enthalpy.

$$H = U + PV \quad \ldots (1)$$

$\Rightarrow$ $dH = dU + PdV + VdP \quad \ldots (2)$

where, H is a state function and dH is an exact differential.

from equation (1)

$$H_1 = U_1 + P_1V_1 \quad \text{and} \quad H_2 = U_2 + P_2V_2$$

$\therefore$ $\Delta H = H_2 - H_1 = (U_2 + P_2V_2) - (U_1 + P_1V_1) = (U_2 - U_1) - (P_2V_2 - P_1V_1)$

$\Delta H = \Delta U + P(V_2 - V_1)$ [At constant pressure $P_2 = P_1 = P$]

$$\boxed{\Delta H = \Delta U + P\Delta V} \quad \ldots (3)$$

Or $\boxed{\Delta H = \Delta U + W}$ $\ldots (4)$

From Ist law

$\Delta U = q - w$

$\therefore$ equation (4) becomes.

$\Delta H = q - w + w$; $\boxed{\Delta H = q_p}$

$\Rightarrow$

If ΔH = +ve, process will be endothermic
If ΔH = −ve, process be will exothermic.

Relation between ΔH & ΔU :

From first law,

$\Delta U = q - w \Rightarrow \Delta U = q - P\Delta V$

at constant volume

$\Delta V = 0 \Rightarrow \boxed{\Delta U = q_V}$

Again we know,

$\Delta H = q_P$

Therefore, from equation (3)

$\Delta H = \Delta U + P\Delta V$

Let n_1 moles of gaseous reactant changes into n_2 mole of gaseous product under constant T and P.

$\therefore$ $PV_1 = n_1RT$; $PV_2 = n_2RT$

$\therefore$ $PV_2 - PV_1 = n_2RT - n_1RT$

$P\Delta V = \Delta n_g RT$ where, Δn_g = (mole of gaseous product) – (moles of gaseous reactant)

$\therefore$ $\boxed{\Delta H = \Delta E + \Delta n_g RT}$ ... (5)

Application of First Law of Thermodynamics:

1. **Heat capacity:** The heat required to raise the temperature by one degree.

It is of two types:

(a) Specific heat capacity: It is the amount of heat absorbed by 1 gm of a substance to raise its temperature by 1°C.

$$\boxed{C = \frac{q}{m(T_2 - T_1)}}$$

(b) Molar heat capacity: It is the amount of heat absorbed by 1 mole of a substance to raise its temperature by 1°C.

$$C = \frac{q}{n(T_2 - T_1)} \quad \Rightarrow C \times n = \frac{q}{(T_2 - T_1)}$$

$$C_M = \frac{q}{(T_2 - T_1)} \Rightarrow \boxed{C = \frac{dq}{dT}}$$

From first law $dq = dU + PdV$

$\therefore$ $$\boxed{C = \frac{dU + PdV}{dT}}$$

(i) At constant volume: **dV= 0**

$$C_V = \left(\frac{dU}{dT}\right)_V \Rightarrow C_V = \left(\frac{\partial U}{\partial T}\right)_V \Rightarrow \boxed{dU = C_V dT}$$

For n moles $\boxed{dU = nC_V dT}$

(ii) At constant pressure:

$$(dq)_P = (dH)_P$$

$$dH = dU + PdV$$

$\because$ $$C_P = \left(\frac{dH}{dT}\right)_P \Rightarrow \boxed{dH = C_p dT}$$

For n mole $\boxed{dH = nC_P dT}$

SOLVED PROBLEMS

1. For the combustion of 1 mole of liquid benzene at 25°C, the heat of reaction at constant pressure is given by

$$C_6H_6(1) + 7\frac{1}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(\ell); \quad \Delta H = -780980 \text{ cal}$$

What would be the heat of reaction at constant volume?

(a) –780 kcal (b) 780 kcal (c) –580 kcal (d) 580 kcal

Soln. We have, $\Delta H = \Delta E + \Delta n_g RT$

Here, $\Delta n_g = 6 - 7.5 = -1.5$

Thus, $\Delta E = \Delta H - \Delta n_g RT = 780980 - (-1.5) \times 2 \times 298 = -780090$ calories $= -780.090$ kcal

Correct option is (a)

2. When 1 mole of ice melts at 0°C and at constant pressure of 1 atm, 1440 calories of heat are absorbed by the system. The molar volumes of ice and water are 0.0196 and 0.0180 litre respectively. Calculate ΔH and ΔE.

Soln. Since, $\Delta H = q_p$

= heat absorbed by the system at constant pressure

= 1440 calories.

In the equation, $\Delta H = \Delta E + p\Delta V$

$$p\Delta V = 76\times13.6\times981(18-19.6) \text{ ergs}$$

$$= -\frac{76\times13.6\times981\times1.6}{4.18\times10^7} \text{ calories}$$

$$= -0.039 \text{ calories}$$

($p = 1$ atm $= 76\times13.6\times981$ dynes/cm^2, $V_2 = 18$ cc, $V_1 = 19.6$ cc)

Since, $p\Delta V$ is very small compared to ΔE, $p\Delta V$ can be neglected.

Thus, $\Delta H = \Delta E = 1440$ calories

3. Show that in an isothermal expansion of an ideal gas (a) $\Delta U = 0$ and (b) $\Delta H = 0$.

Soln. We know that for one mole of an ideal gas, $C_v = \left(\frac{\partial U}{\partial T}\right)_v$, hence, $dU = C_v dT$

For a finite change, $\Delta U = C_v \Delta T$

For an isothermal process, T is constant so that $\Delta T = 0$. Hence, $\Delta U = 0$

(b) We know that, $\Delta H = \Delta U + \Delta(PV)$

Since, for an ideal gas $PV = RT$

$$\Delta H = \Delta U + \Delta(RT) = \Delta U + R\Delta T = R\Delta T \qquad (\because \Delta U = 0)$$

Since, T is constant, $\Delta T = 0$. Hence, $\Delta H = 0$.

4. Calculate q, w, ΔU and ΔH for the reversible isothermal expansion of one mole of an ideal gas 27°C from a volume of 10 dm^3 to a volume of 20 dm^3.

Soln. $T = 27°C = 27 + 273 = 300$ K

Since the process is isothermal,

$$\Delta U = \Delta H = 0$$

$$w = -nRT \ln\left(\frac{V_2}{V_1}\right)$$

$$= -(1 \text{ mol})(8.314 \text{ JK}^{-1}\text{mol}^{-1})(300\text{K}) \text{ in } (20 \text{ dm}^3/10 \text{ dm}^3) = -1729 \text{ J}$$

From the first law, $\Delta U = q + w$

Since, $\Delta U = 0, q = -w = 1729$J

5. Calculate q, w, ΔU and ΔH for the isothermal expansion of one mole of an ideal gas of 27°C from a volume of 10 dm^3 to a volume of 20 dm^3, against a constant external pressure of 1 atm.

Soln. Since, the process is isothermal, $\Delta U = \Delta H = 0$

But, in this case, $w = P(V_2 - V_1) = -(1 \text{ atm})(20 \text{ dm}^3 - 10 \text{ dm}^3)$

$$= -10 \text{ dm}^3\text{atm} = -1013\text{J}$$

Since, $\Delta U = q + w$ and $\Delta U = 0$, hence $q = -w = 1013$J

6. A gas expands isothermally against a constant external pressure of 1 atm from a volume of 10 dm^3 to a volume of 20 dm^3. In this process it absorbs 800J of thermal energy from its surroundings. Calculate the ΔU for the process in joules.

Soln. $w = -\int_{V_1}^{V_2} PdV = -P(V_2 - V_1) = -(1\text{ atm})(20\text{ dm}^3 - 10\text{dm}^3) = -10\text{ dm}^3\text{atm}$

$$= -10\text{ dm}^3 \times \frac{8.314\text{JK}^{-1}\text{mol}^{-1}}{0.08206\text{ dm}^3\text{K}^{-1}\text{mol}^{-1}} = -1013\text{J}$$

From the first law of thermodynamics.

$$\Delta U = q + w = 800\text{J} + (-1013\text{J}) = -213\text{J}$$

Various ($C_P - C_V$) relations:

7. Show that

(i) $C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \cdot \left(\frac{\partial V}{\partial T}\right)_P$ (ii) $C_P - C_V = R$ for ideal gas.

(iii) $C_P - C_V = R\left(1 + \frac{2a}{RTV}\right)$ for real gas (iv) $C_P - C_V = \frac{\alpha^2 TV}{\beta}$

(v) $C_P - C_V = -T\left(\frac{\partial P}{\partial T}\right)_V^2 \left(\frac{\partial V}{\partial P}\right)_T$

Soln. (i) $\boxed{C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \cdot \left(\frac{\partial V}{\partial T}\right)_P}$

Let $S = f(V, T)$

On complete differential

$$dS = \left(\frac{\partial S}{\partial V}\right)_T .dV + \left(\frac{\partial S}{\partial T}\right)_V .dT$$

$$TdS = T\left(\frac{\partial S}{\partial V}\right)_T .dV + T\left(\frac{\partial S}{\partial T}\right)_V .dT$$

We know that, $\left[\left(T\left(\frac{\partial S}{\partial T}\right)_V = C_V\right)\right]$

$$\therefore \quad TdS = T\left(\frac{\partial S}{\partial V}\right)_T .dV + C_V .dT$$

Divide by dT at constant pressure

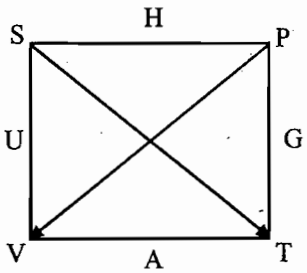
$$\left(\frac{TdS}{dT}\right)_P = T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + C_V \left(\frac{dT}{dT}\right)_P$$

$$C_P = T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + C_V$$

$$C_P - C_V = T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

From thermodynamic square

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$



$$\therefore \quad \boxed{C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \cdot \left(\frac{\partial V}{\partial T}\right)_P}$$

Therefore, the above relation is called as standard equation various relations can be derived by using this rule.

(ii) $\boxed{C_P - C_V = R}$ for ideal gas

From standard equation.

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

$$\therefore \quad C_P - C_V = T\left(\frac{\partial}{\partial T}\frac{RT}{V}\right)_V \left(\frac{\partial}{\partial T}\frac{RT}{P}\right)_P$$

$$C_P - C_V = \frac{TR}{V}\left(\frac{\partial T}{\partial T}\right)_V \times \frac{R}{P}\left(\frac{\partial T}{\partial T}\right)_P = \frac{TR}{V}\cdot\frac{R}{P} = P \times \frac{R}{P}$$

$$\boxed{C_P - C_V = R}$$

[for ideal gas
PV=RT
$P=\frac{RT}{V}$
and $V=\frac{RT}{P}$]

For n mole $\boxed{C_P - C_V = nR}$ Proved.

(iii) $C_P - C_V = R\left(1+\frac{2a}{RTV}\right)$ for real gas:

From standard equation,

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \cdot \left(\frac{\partial V}{\partial T}\right)_p \quad \ldots(1)$$

Now we put value of P and V from van der waal's equation

$$\left(P+\frac{a}{V^2}\right)(V-b) = RT \quad \ldots(2)$$

$$\Rightarrow \quad \left(P+\frac{a}{V^2}\right) = \frac{RT}{(V-b)}; \; P = \left[\frac{RT}{(V-b)} - \frac{a}{V^2}\right]$$

$$\therefore \quad \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial}{\partial T}\frac{RT}{(V-b)}\right)_V - \underbrace{\left(\frac{\partial}{\partial T}\frac{a}{V^2}\right)_V}_{\Downarrow 0}$$

$$\Rightarrow \quad \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{R}{V-b}\right) \quad \ldots(3)$$

Again differentiation equation (2) *w.r.t.* temperature at constant pressure

I II

$$\left[\frac{\partial}{\partial T}\left(P+\frac{a}{V^2}\right)(V-b)\right]_P = \left(\frac{\partial}{\partial T}RT\right)_P$$

$$\Rightarrow \left(P+\frac{a}{V^2}\right)\left[\frac{\partial}{\partial T}(V-b)\right]_P + (V-b)\left(\frac{\partial}{\partial T}P + \frac{a}{V^2}\right)_P = R\left(\frac{\partial T}{\partial T}\right)_P + T\underbrace{\left(\frac{\partial R}{\partial T}\right)_P}_{\Downarrow 0}$$

$$\Rightarrow \left(P+\frac{a}{V^2}\right)\left(\frac{\partial V}{\partial T}\right)_P-\underbrace{\left(\frac{\partial b}{\partial T}\right)_P}_{0}+(V-b)\left[\underbrace{\left(\frac{\partial P}{\partial T}\right)_P}_{0}+\left(\frac{\partial}{\partial T}\frac{a}{V^2}\right)_P\right]=R$$

$$\Rightarrow \left(P+\frac{a}{V^2}\right)\left(\frac{\partial V}{\partial T}\right)_P+(V-b)\left[\frac{-2a}{V^3}\left(\frac{\partial V}{\partial T}\right)_P\right]=R$$

$$\Rightarrow \frac{RT}{(V-b)}\left(\frac{\partial V}{\partial T}\right)_P-\frac{2a}{V^3}(V-b)\left(\frac{\partial V}{\partial T}\right)_P=R$$

$$\left(\frac{\partial V}{\partial T}\right)_P=\frac{R}{\left[\frac{RT}{(V-b)}-\frac{2a(V-b)}{V^3}\right]} \quad \ldots (4)$$

Putting value of equation (3) and (4) in equation (1)

$$C_P-C_V=T\times\frac{R}{(V-b)}\times\frac{R}{\left[\frac{RT}{(V-b)}-\frac{2a(V-b)}{V^3}\right]}$$

$$C_P-C_V=\frac{RT}{(V-b)}\times\frac{R}{\frac{RT}{(V-b)}\left[1-\frac{2a(V-b)^2}{V^3RT}\right]}$$

So, $V>b, (V-b)^2\approx V^2$

$$C_P-C_V=\frac{R}{1-\frac{2aV^2}{V^3RT}}=R\left[1-\frac{2a}{RTV}\right]^{-1} \qquad \text{Let } (V-b\simeq V)$$

$$\boxed{C_P-C_V=R\left[1+\frac{2a}{RTV}\right]} \text{ or } \boxed{C_p-C_v=R\left(1+\frac{2a}{R^2T^2}P\right)} \qquad \textbf{Proved.}$$

(iv) $C_P-C_V=\dfrac{\alpha^2TV}{\beta}$ for ideal gas:

$\because \quad \alpha=\dfrac{1}{V}\left(\dfrac{\partial V}{\partial T}\right)_P, \qquad \beta=-\dfrac{1}{V}\left(\dfrac{\partial V}{\partial P}\right)_T$

$$\therefore \quad C_P-C_V=\frac{\left[\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P\right]^2\times T\times V}{-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T}=\frac{\frac{1}{V^2}\left(\frac{\partial V}{\partial T}\right)_P^2\times T\times V}{-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T}$$

$$C_P-C_V=-T\left(\frac{\partial V}{\partial T}\right)_P\cdot\underbrace{\left(\frac{\partial V}{\partial T}\right)_P\cdot\left(\frac{\partial P}{\partial V}\right)_T}$$

From cyclic rule.

$$\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial T}{\partial P}\right)_V\left(\frac{\partial P}{\partial V}\right)_T=-1 \quad \Rightarrow \left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial V}\right)_T=-\frac{1}{\left(\frac{\partial T}{\partial P}\right)_V}$$

$$\therefore \quad C_P-C_V=-T\left(\frac{\partial V}{\partial T}\right)_P\times-\left(\frac{\partial P}{\partial T}\right)_V=T\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial T}\right)_V$$

Thus standard rule proves validity of given relation.

(v) $C_P-C_V=-T\left(\frac{\partial P}{\partial T}\right)^2\left(\frac{\partial V}{\partial P}\right)_T$

From fundamental rule.

$$C_P-C_V=T\left(\frac{\partial V}{\partial T}\right)_P\cdot\left(\frac{\partial P}{\partial T}\right)_V$$

From cyclic rule.

$$\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P\cdot\left(\frac{\partial T}{\partial P}\right)_V=-1 \quad \Rightarrow\left(\frac{\partial V}{\partial T}\right)_P=\frac{-1}{\left(\frac{\partial P}{\partial V}\right)_T\cdot\left(\frac{\partial T}{\partial P}\right)_V}$$

$$\left(\frac{\partial V}{\partial T}\right)_P=-\left(\frac{\partial V}{\partial P}\right)_T\cdot\left(\frac{\partial P}{\partial T}\right)_V$$

Using Euler's theorem, $1/\left(\frac{\partial P}{\partial V}\right)_T=\left(\frac{\partial V}{\partial P}\right)_T$

$$\therefore \quad C_P-C_V=T\left[-\left(\frac{\partial V}{\partial P}\right)_T\cdot\left(\frac{\partial P}{\partial T}\right)_V\right]\left(\frac{\partial P}{\partial T}\right)_V$$

$$\boxed{C_P-C_V=-T\left(\frac{\partial V}{\partial P}\right)_T\cdot\left(\frac{\partial P}{\partial T}\right)_V^2}$$ Proved.

8. Calculate C_P-C_V for nitrogen at 298K and 100 bar pressure, the van der waals constant '*a*' is 141 dm^6 kPa mol^{-2}.

Soln. We have,

$p = 100 \text{ bar} = 10^4 \text{ kPa}$

$a = 141 \text{ dm}^6 \text{ kPa mol}^{-2}$

For a gas obeying van der Waals equation, we have

$$C_P-C_V=R\left(1+\frac{2a}{R^2T^2}P\right)$$

Substituting the given values, we get

$$C_P-C_V=\left(8.314\text{ JK}^{-1}\text{mol}^{-1}\right)\times\left(1+\frac{2\left(141\text{ dm}^6\text{kPamol}^{-2}\right)}{\left(8.314\text{ dm}^3\text{ kPaK}^{-1}\text{mol}^{-1}\right)^2\left(298\text{K}\right)^2}\right)$$

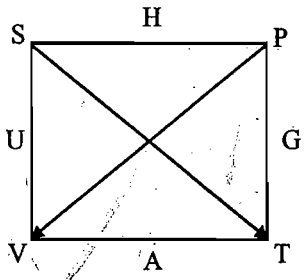
$$=\left(8.314\text{ JK}^{-1}\text{mol}^{-1}\right)\left(1+0459\right)=12.13\text{ JK}^{-1}\text{mol}^{-1}$$

First Thermodynamic Equation of State

Change in internal energy with respect to volume at constant temperature is known as first thermodynamic equation of state i.e. $\left(\frac{\partial U}{\partial V}\right)_T$

Dimensionally it was seen that its dimension is the dimension of pressure. Thus it is also called as internal pressure (π_T)

From thermodynamic square



$$dU = TdS - PdV$$

$$\therefore \quad \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P\left(\frac{\partial V}{\partial V}\right)_T$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$$

From thermodynamic square

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$\Rightarrow \quad \boxed{\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P}$$

Or $$\boxed{\pi_T = T\left(\frac{\partial P}{\partial T}\right)_V - P} \qquad \ldots (1)$$

For ideal gas internal pressure (π_T) is zero.

From equation (1)

$$\pi_T = T\left(\frac{\partial}{\partial T}\frac{RT}{V}\right)_V - P = T\frac{R}{V}\left(\frac{\partial T}{\partial T}\right)_V - P = \frac{RT}{V} - P = P - P = 0 \Rightarrow \pi_T = 0 \text{ for ideal gas}$$

For real gas internal pressure (π_T) is $\frac{a}{V_2}$:

For real gas; $\left(P + \frac{a}{V^2}\right)(V-b) = RT \Rightarrow P = \left[\left(\frac{RT}{V-b}\right) - \frac{a}{V^2}\right]$

So, from equation (1), we get.

$$\therefore \quad \pi_T = T\left(\frac{\partial}{\partial T}\frac{RT}{(V-b)}\right)_V - \left(\frac{\partial}{\partial T}\underbrace{\frac{a}{V^2}}_{\Downarrow 0}\right)_V - P = T\frac{R}{(V-b)}\left(\frac{\partial T}{\partial T}\right)_V - P$$

$$= \frac{RT}{(V-b)} - P = \left(P + \frac{a}{V^2}\right) - P \qquad \left[\because \left(P + \frac{a}{V^2}\right) = \frac{RT}{(V-b)}\right]$$

$$\boxed{\pi_T = \frac{a}{V^2}}$$

For n moles,

$$\boxed{\pi_T = \frac{n^2 a}{V^2}}$$

Second Thermodynamic Equation of State

Change in enthalpy w.r.t pressure at consant temperature is known as second thermodynamic equation of state.

$$dH = TdS + VdP$$

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V\left(\frac{\partial P}{\partial P}\right)_T \Rightarrow \left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V$$

From thermodynamic square,

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

$$\therefore \left(\frac{\partial H}{\partial P}\right)_T = \left[-T\left(\frac{\partial V}{\partial T}\right)_P + V\right] \quad \ldots (1)$$

For ideal gas $\left(\frac{\partial H}{\partial P}\right)_T = 0$

$$\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial}{\partial T}\frac{RT}{P}\right)_P + V = -T\frac{R}{P}\left(\frac{\partial T}{\partial T}\right)_P + V = -V + V \Rightarrow \left(\frac{\partial H}{\partial P}\right)_T = 0$$

Problem: Show that for fixed amount of ideal gas $\left(\frac{\partial C_V}{\partial V}\right)_T = 0$

Soln. $\left(\frac{\partial C_V}{\partial V}\right)_T = \left[\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_V\right]_T$

Changing the operator and U is a state function.

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \left[\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_T\right]_V, \quad \text{but } \left(\frac{\partial U}{\partial V}\right)_T = 0 \text{ for ideal gas}$$

$$\therefore \quad \left(\frac{\partial C_V}{\partial V}\right)_T = 0 \qquad \text{proved.}$$

Variation of heat of reaction temperature:

For low range of temperature, two relations are

$$\Delta C_P \qquad \frac{\Delta H_2}{T_2} \qquad \frac{\Delta H_1}{T_1}$$

$$\Delta C_V \qquad \frac{\Delta E_2}{T_2} \qquad \frac{\Delta E_1}{T_1}$$

Consider the equation, $aA + bB \rightarrow cC + dD$

(Where, a, b, c and d are stoichiometric Coefficients)

$$\Delta H = \sum H_P - \sum H_R$$

$$\Rightarrow \quad \Delta H = (cH_C + dH_D)_{\text{product}} - (aH_A + bH_B)_{\text{reactant}}$$

$$\Rightarrow \quad \left[\frac{\partial(\Delta H)}{\partial T}\right]_P = \left[c\left(\frac{\partial H_C}{\partial T}\right)_P + d\left(\frac{\partial H_D}{\partial T}\right)_P\right]_{\text{Product}} - \left[a\left(\frac{\partial H_A}{\partial T}\right)_P + b\left(\frac{\partial H_B}{\partial T}\right)_P\right]_{\text{Reactant}}$$

$$\Rightarrow \quad \left(\frac{\partial(\Delta H)}{\partial T}\right)_P = \left[\underset{\text{Specific heat Capacities of Product}}{c\,C_P(C) + d\,C_P(D)}\right]_{\text{Product}} - \left[\underset{\text{Specific heat Capacities of Reactant}}{a\,C_P(A) + b\,C_P(B)}\right]_{\text{Reactant}}$$

$$\Rightarrow \quad \left[\frac{\partial(\Delta H)}{\partial T}\right]_P = (C_P)_{\text{Product}} - (C_P)_{\text{Reactant}}; \quad \left[\frac{\partial(\Delta H)}{\partial T}\right]_P = \Delta C_P; \quad d(\Delta H) = \Delta C_P\, dT$$

$$\Rightarrow \quad \int_{T_1}^{T_2} d(\Delta H) = \int_{T_1}^{T_2} \Delta C_P dT \qquad \ldots (i)$$

If at $T = T_1$, $\Delta H = \Delta H_1$ and $T = T_2$, $\Delta H = \Delta H_2$
then from equation (i)

$$\Rightarrow \quad \Delta H_2 - \Delta H_1 = \Delta C_P (T_2 - T_1)$$

$$\Rightarrow \quad \boxed{\Delta H_2 = \Delta H_1 + \Delta C_P (T_2 - T_1)} \qquad \ldots (ii)$$

Similarly, $\boxed{\Delta E_2 = \Delta E_1 + \Delta C_V (T_2 - T_1)}$ ... (iii)

Equation (ii) and (iii) are known as 'Kirchoff's equations'.

9. The enthalpy of reaction ΔH for the formation of ammonia according to the reaction

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

at 27°C was found to be – 91.94 kJ.
What willbe the enthalpy of reaction ΔH at 50°C?
Molar heat capacities at constant pressure and at 27°C for N_2, H_2 and NH_3 are 28.45, 28.32 & 37.07 Joules/ K respectively,

Soln: From Kirchoff's equation we have

$$\Delta H_2 = \Delta H_1 + \Delta C_P (T_2 - T_1) \qquad \ldots (i)$$

Here $T_1 = 27°C = (27 + 273)\ K = 300K$ ... (ii)

$T_2 = 50°C = (50 + 273)\ K = 323\ K$ ... (iii)

$\Delta H_1 = -91.94\ K.J = -91.94 \times 10^3 J$ ... (iv)

$\Delta C_P = 2C_P(NH_3) - [C_P(N_2) + 3\,C_P(H_2)]$ ... (v)

$$\Rightarrow \quad \Delta C_P = 2 \times 37.07\ J/K - [28.45 + 3 \times 28.32]\ J/K \qquad \ldots (v)$$

$$\Rightarrow \quad \Delta C_P = -39.27\ /J/K \text{ and } \Delta H_2 = ? \qquad \ldots (vi)$$

Now making substitution from the equation (ii), (iii) (iv) and (v) in equation (i), we get

$$\Delta H_2 = -91.94 \times 10^3\ J + (-39.27)\ [323 - 300)] = -91.94 \times 10^3\ J - 39.27 \times 23\ J$$
$$= -91.94 \times 10^3\ J - 903.21\ J = -92843.21\ J = -92.843\ kJ$$

10. Prove that for reversible process $\oint w = 0$

Soln. Let a gas is expanding from an initial volume of V_1 to a final volume V_2.
Thus reversible work

$$w_1 = -2.303RT \log \frac{V_2}{V_1}$$

Now the gas is compressed from $V_2 \rightarrow V_1$

$$w_2 = -2.303RT \log \frac{V_1}{V_2} = 2.303RT \log \frac{V_2}{V_1}$$

$\therefore$ Total cyclic work.

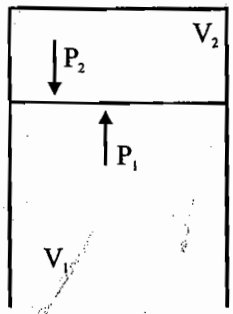
$$\oint w = w_1 + w_2 = -2.303RT \log \frac{V_2}{V_1} + 2.303RT \log \frac{V_2}{V_1} = 0$$

So, $\oint w = 0$

11. Prove that For irreversible process $\oint w \neq 0$

Soln. Let a gas expanding irreversibly from $V_1 \rightarrow V_2$ against external pressure P_2.

$$w_{exp} = -P_2 \text{ ext}(V_2 - V_1)$$



$$\therefore \quad \oint w = w_1 + w_2$$

$$= -P_2(V_2 - V_1) - P_1(V_1 - V_2)$$

$$= -p_2(V_2 - V_1) + P_1(V_2 - V_1)$$

$$\oint w = (V_2 - V_1) + (P_1 - P_2)$$

w_{irr} = +ive value

So, $\oint w \neq 0$

12. Show that for an ideal gas

(a) $\left(\frac{\partial U}{\partial V}\right)_T = 0$ (b) $\left(\frac{\partial H}{\partial P}\right)_T = 0$ (c) $\left(\frac{\partial U}{\partial P}\right)_T = 0$ (d) $\left(\frac{\partial H}{\partial V}\right)_T = 0$

Soln. (a) For an ideal gas, $PV = nRT$ or $P = nRT/V$

$$\therefore \quad \left(\frac{\partial P}{\partial T}\right)_V = nR/V = P/T$$

Substituting this value in the first thermodynamics equation of state, we have

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P = T\left(\frac{P}{T}\right) - P = 0$$

(b) For an ideal gas, $PV = nRT$ or $V = \frac{nRT}{P}$

$$\therefore \quad \left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P} = \frac{V}{T}$$

Substituting this value in the Second thermodynamics equation of state, we have

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P = V - T\left(\frac{V}{T}\right) = 0$$

(c) Since, $H = U + PV$, hence, $U = H - PV = H - nRT$

Or, $$\left(\frac{\partial U}{\partial P}\right)_T = \left(\frac{\partial (H - nRT)}{\partial P}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T - \left(\frac{\partial (nRT)}{\partial P}\right)_T = 0 - 0 = 0$$

(d) Since, $H = U + PV = U + nRT$

$$\therefore \quad \left(\frac{\partial H}{\partial V}\right)_T = \left(\frac{\partial (U + nRT)}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T + \left(\frac{\partial (nRT)}{\partial V}\right)_T = 0 + 0 = 0$$

Thermodynamics changes in isothermal variation in volume of an ideal gas :

Expression for q, w, ΔH and ΔH :

We shall use the first law of thermodynamics to calculate the changes in thermodynamics properties when an ideal gas undergoes the process of expansion or compression.

In an isothermal expansion or compression process, the temperature of the system remains constant throughout the expansion or compression process. Since for an ideal gas, U depends only on temperature (Joule's law, $\left(\frac{\partial U}{\partial V}\right)_T = 0$), it follows that

$$\boxed{dU = 0 \text{ or } \Delta U = 0}$$

Substituting the above expression in the first law of thermodynamics, we get

$$dq = -dw \text{ or } q = -w$$

Hence, in an isothermal expansion or compression process, heat is converted into work and vice versa. Thus, if heat is supplied to the sytsem (q positive), the equivalent amount of work is done by the system (w negative), and if some work is done on the system. (w positive), the equivalent amount of heat is given out (q negative)

The enthalpy change of the sytsem is also zero as

$$\Delta H = \Delta(U + pV) = \Delta U + \Delta(pV)$$

$$= \Delta U + \Delta(nRT) = \Delta U + nR(\Delta T) = 0 + 0 = 0$$

The magnitude of w (or q) depens on how the expansion or compression process is carried out. Two different types of processes may be distinguished, namely, reversible and irreversible.

Reversible Expansion or Compression Process :

The expansion for the work involved in an isothermal expansion or compression from volume V_1 to V_2 can be worked out as follows :

Sine, $dw = -p_{opp}dV$, therefore,

$$w = -\int_{V_1}^{V_2} p_{opp}dV$$

In the reversible change of volume, the opposite pressure differs from the pressure of the gas by an infinitesimal amount, i.e.

$$p_{opp} = p_{\text{int}} \pm dp$$

where +ve and –ve signs are meant for compression and expansion processes, respectively.
Substituting this is the previous expression, we get

$$w = -\int_{V_1}^{V_2}(p_{\text{int}} \pm dp)\,dV = -\int_{V_1}^{V_2} p_{\text{int}}dV \mp \int_{V_1}^{V_2} dpdV$$

The second integration can be neglected, since it is product of two infinitesimal small differentiable. For an ideal gas, p_{int} is given by

$$p_{\text{int}} = \frac{nRT}{V}$$

with this the previous expression becomes

$$w = -\int_{V_1}^{V_2}\frac{nRT}{V}dV$$

Since temperature remains constant in an isothermal process, we have

$$w = -nRT\int_{V_1}^{V_2}\frac{dV}{V} = -nRT\ln\frac{V_2}{V_1}$$

In terms of pressure, we have

$$w = -nRT \ln \frac{p_1}{p_2}$$

Hence, for an isothermal reversible expansion or compression, we have

$$\boxed{q = -w = nRT \ln \frac{V_2}{V_1} = nRT \ln \frac{p_1}{p_2}}$$

$$\Delta U = \Delta H = 0$$

PROBLEMS

1. What is the work which could be obtained from an isothermal reversible expansion of 1 mol of Cl_2 from 1 dm^3 to 50 dm^3 at 273K using ideal gas behaviour.
(a) –8.88 kJ mol^{-1} (b) 8.88 kJ mol^{-1} (c) –88.8 kJ mol^{-1} (d) 88.8 kJ mol^{-1}

Soln. For an ideal gas

$$w = -RT \ln \frac{V_2}{V_1}$$

$$= -\left(8.314 JK^{-1} mol^{-1}\right)(273K) \times 2.303 \times \log\left(\frac{50 dm^3}{1 dm^3}\right)$$

$$= -8.880 J\ mol^{-4} = -8.88\ kJ\ mol^{-1}$$

Correct option is (a)

2. One dm3 of an ideal gas at a pressure of 1.013 3 MPa expands reversibly and isothermally from its volume to 10 dm^3. How much of heat is absorbed and work is done in expansion?

Soln. For an ideal gas undergoing reversible volume change, we have

$$q = -w = nRT \ln \frac{V_2}{V_1}$$

The temperature in the above expression can be replaced in terms of p_1 and V_1 by using the ideal gas equation. Thus,

$$q = (p_1 V_1) \ln \frac{V_2}{V_1}$$

Substituting the value of p_1, V_1 and V_2, we have

$$q = (1.013\,3 Mpa)\left(1 dm^3\right) \times 2.303 \times \log\left(\frac{10\ dm^3}{1\ dm^3}\right)$$

$$= 2.333\,6\ Mpa\ dm^3 = 2.333\,6 kJ$$

Irreversible Expansion or Compression process :

Two types of irreversible change in volume may be distinguished, namely, expansion against a zero pressure (free expansion) and expansion or compression against a constant pressure (intermediate expansion or compression). The change in q, w, ΔU and ΔH for these processes are given below.

For free expansion, $p_{opp} = 0$

Therefore, $w = \int dw = -\int p_{opp} dV = 0$

Thus, $q = -w = 0$

$\Delta U = \Delta H = 0$

Intermediate expansion or compression :

Here, the work is done against a constant external pressure.

Therefore, $$w = -\int_{V_1}^{V_2} p_{opp}\, dV = -p_{opp}(V_2 - V_1)$$

Hence, in the present case, we have

$$q = -w = p_{opp}(V_2 - V_1)$$

$$\Delta U = \Delta H = 0$$

Comparison between reversible isothermal and adiabatic expansion of an ideal gas:

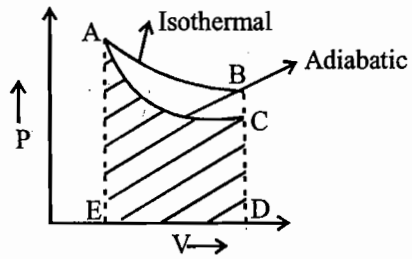
Comparison of the Isothermal curve and Adiabatic curve :

It is clear from the curve that the work done in isothermal process is greater than that in adiabatic process is greater than that in adiabatic process since the area (ABDE) under the curve (AB) for the isothermal process is more than the area (ACDE) under the curve (AC) for the adiabatic process.

i.e, $W_{ABDE} = W_{ABC} + W_{ACDE}$

$\Rightarrow$ $W_{iso} = W_{ABC} + W_{adia}$

$\Rightarrow$ $\boxed{W_{iso} > W_{adia}}$



Prove that if the final volume of the gas in isothermal and adiabatic process is same, then the final pressure of the gas in isothermal process will be more than that in adiabatic process.

i.e $P_{iso} > P_{adia}$ or $(P_f)_{iso} > (P_f)_{adia}$

Proof : Let P_i be the initial pressure of the gas in both the process (viz isothermal and adiabatic) and let V_i be the initial volume of the gas in both the processes (viz isothermal and adiabatic).

Let V_f be the final volume of the gas in both the processes (viz isothermal and adiabatic). Let P_{iso} be the final pressure of the gas in isothermal process and let P_{adia} be the final pressure of the gas in adiabatic process.

Isothermal Process : For isothermal process, we know that PV= Constant

$\Rightarrow$ $P_1V_1 = P_2V_2 \Rightarrow P_iV_i = P_{iso}V_f$

$\Rightarrow$ $$\boxed{\frac{P_i}{P_{iso}} = \frac{V_f}{V_i}} \quad \ldots (1)$$

Adiabatic Process:

For adiabatic Process we know that

PV^γ = constant

$\Rightarrow$ $P_1V_1^\gamma = P_2V_2^\gamma \Rightarrow P_iV_i^\gamma = P_{adia}V_f^\gamma$

$\Rightarrow$ $$\frac{P_i}{P_{adia}} = \left(\frac{V_f}{V_i}\right)^\gamma \quad \ldots (2)$$

From (1) and (2), we have, $\frac{P_i}{P_{adia}} = \left(\frac{P_i}{P_{iso}}\right)^{\gamma}$ ... (3)

Since $V_f > V_i \Rightarrow \frac{V_f}{V_i} > 1 \Rightarrow \left(\frac{P_i}{P_{iso}}\right) > 1$ and also γ is always greater than 1 (i.e. $\gamma > 1$).

Therefore, we have from equation (3)

$$\frac{P_i}{P_{adia}} > \frac{P_i}{P_{iso}} ; \frac{1}{P_{adia}} > \frac{1}{P_{iso}} \quad [\because P_i > 0]$$

$\Rightarrow$ $\boxed{P_{iso} > P_{adia}}$

i.e The final pressure of the gas in isothermal process is more than that in adiabatic process.

Prove that if the final pressure of the gas in isothermal and adiabatic process is same, then the final volume of the gas in isothermal process will be more than that in adiabatic process.

i.e $V_{iso} > V_{adia}$ OR $(V_f)_{iso} > P_{adia}$

In this case also $\boxed{W_{iso} > W_{adia}}$

Let P_i be the initial pressure of the gas in both the processes (viz isothermal and adiabatic) & Let P_f be the final pressure of the gas in both the process (viz isothermal and adiabatic).

Let V_i be the initial volume of the gas in both the processes (viz isothermal and adiabatic).

Let V_{iso} be the final volume of the gas in isothermal process and let V_{adia} be the final volume of the gas in adiabatic process.

Isothermal Process :

For isothermal process, we know that PV= constant

$\Rightarrow$ $P_1V_1 = P_2V_2 \Rightarrow P_iV_i = P_fV_{iso}$

$\Rightarrow$ $\boxed{\frac{V_{iso}}{V_i} = \frac{P_i}{P_f}}$ ... (i)

Adiabatic Process:

For adiabatic process, we know that

PV^{γ} = constant

$\Rightarrow$ $P_1V_1^{\gamma} = P_2V_2^{\gamma}$; $P_iV_i^{\gamma} = P_fV_{adia}^{\gamma}$; $\left(\frac{V_{adia}}{V_i}\right)^{\gamma} = \frac{P_i}{P_f}$; $\frac{V_{adia}}{V_i} = \left(\frac{P_i}{P_f}\right)^{\frac{1}{\gamma}}$ ... (ii)

From (i) and (ii), we have $\frac{V_{adia}}{V_i} = \left(\frac{V_{iso}}{V_i}\right)^{\frac{1}{\gamma}}$

Taking log on both the sides, we get

$$\log_{10}\left(\frac{V_{adia}}{V_i}\right) = \frac{1}{\gamma}\log_{10}\left(\frac{V_{iso}}{V_i}\right) \Rightarrow \log_{10}\left(\frac{V_{iso}}{V_i}\right) = \gamma\log_{10}\left(\frac{V_{adia}}{V_i}\right) \quad \text{... (iii)}$$

Now since, $V_{iso} > V_i \Rightarrow \frac{V_{iso}}{V_i} > 1 \Rightarrow \log\left(\frac{V_{iso}}{V_i}\right) > 0$

And $V_{adia} > V_i \Rightarrow \frac{V_{adia}}{V_i} > 1 \Rightarrow \log\left(\frac{V_{adia}}{V_i}\right) > 0$

And $\boxed{\text{Also, } \gamma > 1}$

Therefore it is clear from the Equation (iii)

$$\log\left(\frac{V_{iso}}{V_i}\right) > \log\left(\frac{V_{adia}}{V_i}\right) \Rightarrow \frac{V_{iso}}{V_i} > \frac{V_{adia}}{V_i}$$

$\Rightarrow$ $\boxed{V_{iso} > V_{adia}}$ $[\because V_i > 0]$

i.e The final volume of the gas in isothermal process is more than that in adiabatic process.

Combined Result of (6), (7), (8) and (9)

$$\boxed{(\text{Slope})_{adiabatic} = \gamma\,(\text{Slope})_{isothermal}}$$

$$\boxed{W_{isothermal} > W_{adiabatic}}$$

When final volume of the gas in same in both the process (viz isothermal and adiabatic), Then

$$\boxed{(P_{final})_{isothermal} > (P_{final})_{adiabatic}}$$

When final pressure of the gas is same in both the processes (viz isothermal and adiabatic), then

$$\boxed{(V_{final})_{isothermal} > (V_{final})_{adiabatic}}$$

Joule-Thomson Effect

Porus Plug Experiment:

When any gas is subjected from a higher pressure region to a lower pressure region through a porus plug adiabatically, cooling takes place except for H_2 and He. At the same conditions of temp and pressure when these gases are subjected from a higher pressure region to a lower pressure region through a porus plug adiabatically, heating takes place.

This effect is known as 'Joule-Thomson effect'. It is an isoenthalpic and adiabatic process.

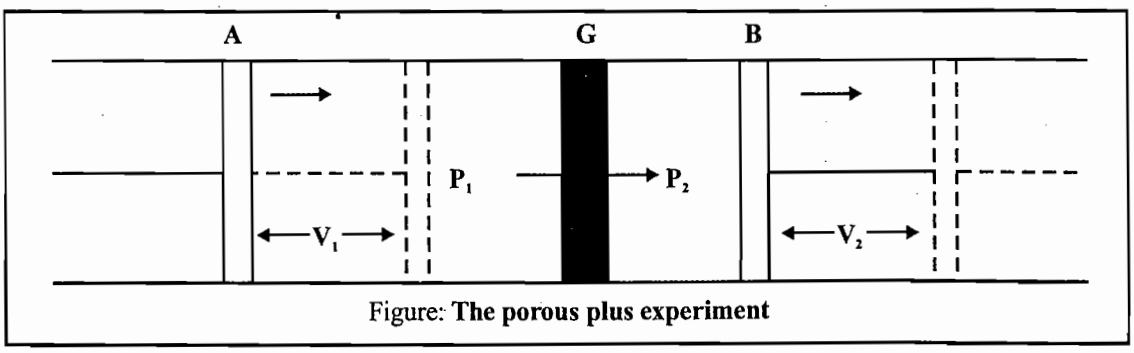


Figure: **The porous plus experiment**

Since Joule-Thomson effects is an adiabatic Process, therefore,

$dQ = dU + dW$

$\Rightarrow$ $0 = dU + dW; -dW = dU$ $(\because dQ = 0)$ ... (1)

i.e. the work done by the gas is equal to the change in internal energy.

$\Rightarrow \quad -PdV = dU$

$\Rightarrow \quad -P(V_2 - V_1) = U_2 - U_1$

$\Rightarrow \quad -PV_2 + PV_1 = U_2 - U_1$

$\Rightarrow \quad U_1 + PV_1 = U_2 + PU_2$

$\Rightarrow \quad H_1 = H_2$

$\Rightarrow \quad H_2 - H_1 = 0$

$\Rightarrow \quad \Delta H = 0 \qquad \Rightarrow dH = 0$

H = constant

$\Rightarrow$ Joule-Thomson effect is an isoenthalpic process

Joule Thomson Coefficient:

$H = H(T, P)$

$$\Rightarrow \quad dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

$$\Rightarrow \quad 0 = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \quad [\because \text{In Joule-Thomson effect } dH = 0]$$

$$\Rightarrow \quad 0 = C_P\, dT + \left(\frac{\partial H}{\partial P}\right)_T dP \Rightarrow C_P\, dT = -\left(\frac{\partial H}{\partial P}\right)_T dP \Rightarrow \left(\frac{dT}{\partial P}\right)_H = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T$$

$$\Rightarrow \quad \boxed{\left(\frac{dT}{dP}\right)_H = -\frac{1}{C_P}\left(\frac{dH}{dP}\right)_T}$$

$\left(\frac{\partial T}{\partial P}\right)_H$ is known as Joule-Thomson coefficient and is denoted by $\mu_{J.T.}$ (Joule Thomson Coefficient)

$$\mu_{J.T} = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T \qquad \ldots (1)$$

From thermodynamic square.

$dH = TdS + VdP$

$$\therefore \quad \left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V\left(\frac{\partial P}{\partial P}\right)_T$$

Again, $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

$$\therefore \quad \mu_{J.T} = -\frac{1}{C_P}\left[-T\left(\frac{\partial V}{\partial T}\right)_P + V\right]$$

$$\boxed{\mu_{J.T} = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]} \qquad \ldots (2)$$

Joule-Thomson Coefficient and Ideal gas equation of state :

The expression for Joule-Thomsen coefficient as given by

$$\mu_{J.T}=\frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P-V\right]=\frac{1}{C_P}\left[T\left(\frac{\partial}{\partial T}\frac{RT}{P}\right)_P-V\right]=\frac{1}{C_P}\left[\frac{R}{P}T\left(\frac{\partial T}{\partial T}\right)_P-V\right]$$

$$=\left[\frac{T}{C_P}\frac{R}{P}-\frac{V}{C_P}\right]=\frac{V}{C_P}-\frac{V}{C_P}=\frac{1}{C_P}(V-V)$$

$\therefore$ $\boxed{\mu_{J.T}=0}$ for ideal gas

Joule-Thomson Coefficient and vander Waal equation of state :

The expression for Joule-Thomsen coefficient as given by

$$\mu_{J.T}=\frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P-V\right] \qquad \ldots (1)$$

We have to find value of $\left(\frac{\partial V}{\partial T}\right)_P$ for real gas and put it into above equation.

$$\underset{I}{\quad}\quad \underset{II}{\quad}\quad\quad \underset{I}{\quad}\ \underset{II}{\quad}$$

$$\frac{\partial}{\partial T}\left[\left(P+\frac{a}{V^2}\right)(V-b)\right]_P=\frac{\partial}{\partial T}(R\ T)_P$$

$$\Rightarrow \quad \left(P+\frac{a}{V^2}\right)\frac{\partial}{\partial T}(V-b)_P+(V-b)\frac{\partial}{\partial T}\left(P+\frac{a}{V^2}\right)_P=R\left(\frac{\partial T}{\partial T}\right)_P+T\left(\frac{\partial R}{\partial T}\right)_P$$

$$\Rightarrow \quad \left(P+\frac{a}{V^2}\right)\left(\frac{\partial V}{\partial T}\right)_P-\left(\frac{\partial b}{\partial T}\right)_P+(V-b)\left[\left(\frac{\partial P}{\partial T}\right)_P+\left(\frac{\partial}{\partial T}\frac{a}{V^2}\right)_P\right]=R$$

$$\Rightarrow \quad \left(P+\frac{a}{V^2}\right)\left[\left(\frac{\partial V}{\partial T}\right)_P-\left(\frac{\partial b}{\partial T}\right)_P\right]+(V-b)\left[\left(\frac{\partial P}{\partial T}\right)_P+\left(\frac{\partial a}{\partial T V^2}\right)_P\right]=R$$

$$\Rightarrow \quad \left(P+\frac{a}{V^2}\right)\left[\left(\frac{\partial V}{\partial T}\right)_P-0\right]+(V-b)\left[0+\frac{-2a}{V^3}\left(\frac{\partial V}{\partial T}\right)_P\right]=R$$

$$\Rightarrow \quad \left(P+\frac{a}{V^2}\right)\left(\frac{\partial V}{\partial T}\right)_P+(V-b)-\frac{2a}{V^3}\left(\frac{\partial V}{\partial T}\right)_P \Rightarrow \left(\frac{\partial V}{\partial T}\right)_P\left[\left(P+\frac{a}{V^2}\right)-\frac{2a}{V^3}(V-b)\right]=R$$

$$\Rightarrow \quad \left(\frac{\partial V}{\partial T}\right)_P\left[\left(\frac{RT}{(V-b)}\right)-\frac{2a}{V^3}(V-b)\right]=R$$

$$\Rightarrow \quad \left(\frac{\partial V}{\partial T}\right)_P\left[\frac{RT}{V-b}-\frac{2a(V-b)}{V^3}\right]=R \qquad \left[\left(P+\frac{a}{V^2}\right)=\frac{RT}{(V-b)}\right]$$

$$\left(\frac{\partial V}{\partial T}\right)_P=\frac{R}{\frac{RT}{(V-b)}\left[1-\frac{2a(V-b)^2}{V^3RT}\right]} \qquad \ldots (2)$$

Putting value of equation (2) in equation (1)

$$\mu_{J.T}=\frac{1}{C_P}\left[\frac{TR}{\frac{RT}{V-b}\left[1-\frac{2aV^2}{V^3RT}\right]}-V\right]=\frac{1}{C_P}\left[V+\frac{2av}{RTV}-b-\underset{\text{neglected}}{\frac{2ab}{RTV}}-V\right] \qquad [V-b\simeq V]$$

$$\mu_{J,T}=\frac{1}{C_P}\left[(V-b)\left(1-\frac{2a}{RTV}\right)^{-1}-V\right]$$

$$\left[\text{so},\left(1-\frac{2a}{RTV}\right)^{-1}=\left(1+\frac{2a}{RTV}\right)\right] \qquad \left(\frac{2ab}{RTV}\text{ is very small may be neglected}\right)$$

$$\boxed{\mu_{J.T}=\frac{1}{C_P}\left[\frac{2a}{RT}-b\right]}$$

Inversion temperature (T_i):

The temperature at which $\mu_{J.T}$ becomes zero i.e. neither heating nor cooling takes place and gas behaves ideally is called inversion temperature.

$$\mu_{J.T}=\left(\frac{\partial T}{\partial P}\right)_H=\frac{1}{C_P}\left[\frac{2a}{RT}-b\right]$$

If $\mu_{J.T}=0$, $T=T_i$

$$\Rightarrow \qquad 0=\frac{1}{C_P}\left[\frac{2a}{RT_i}-b\right]\Rightarrow\frac{2a}{RT_i}-b=0\Rightarrow\frac{2a}{RT_i}=b$$

$$\boxed{T_i=\frac{2a}{Rb}} \qquad \ldots (3)$$

Now following experimental condition indicates heating or cooling.
During J.T. effect.

$$dP=-ve \qquad \therefore \qquad \mu_{J.T}=\left(\frac{\partial T}{\partial P}\right)_H$$

If $\mu_{J.T}$ = positive then ∂T should be negative, $T_2<T_1$
Thus cooling takes place.

In experimental condition:

$$\mu_{J.T}=\frac{1}{C_P}\left[\frac{2a}{RT}-b\right] \qquad \text{If } \mu_{J.T}=+ve \text{ means } \mu_{J,T}>0$$

$$\Rightarrow \qquad 0<\frac{1}{C_P}\left[\frac{2a}{RT}-b\right];\left(\frac{2a}{RT}-b\right)>0;\left(\frac{2a}{RT}-b\right)>0;\frac{2a}{Rb}>T$$

$$\boxed{T_i>T}$$

Thus experimental temperature should be lesser than the inversion temperature of a gas for cooling.

2. **If $\mu_{J.T}$ = negative:**

Thus ∂T should be positive

$\therefore \qquad T_2-T_1>0;\ T_2>T_1$ (heating takes place)

In experiemental condition:

$$0 > \frac{1}{C_P}\left[\frac{2a}{RT} - b\right] \Rightarrow \frac{2a}{RT} < b \Rightarrow \frac{2a}{Rb} < T \Rightarrow T_i < T \quad [T = \text{experimental temperature}]$$

If experimetnal temperature is greater than T_i heating takes during J.T. experiement.

Note: H_2 and He gases have a very low T_i (–80°C and –240°C). This temperature is always below the experiemental condition temperature, thus heating happen.

Joule-Thomson Coefficient for a Real gas :

Joule-Thomson coefficient may be positive or negative or zero depending upon the temperature and pressure of the gas. Since the change in pressure, dp, in Joule-Thomson experiment is always negative, it follows that dT is negative when μ_{JT} is positive, and vice-versa, the effects are summarized in table below.

Experimental result	μ_{JT}	$\left(\frac{\partial H}{\partial P}\right)_T$	Comments
dT negative, i.e. $T_2 < T_1$ Cooling	(+)	(–)	Most gases, H_2 and He at low temperature.
dT zero, i.e. $T_2 = T_1$ Neither heating nor cooling	Zero	Zero	Ideal gas, real gas at inversion temperature
dT positive i.e., $T_2 > T_1$ Heating	(–)	(+)	Most gases at high temperature H_2 and He at ordinary temperature.

3. Calculate the Joule-Thomson coefficient of carbon monoxide at 298K and 40.53 MPa pressure, given that $\left(\frac{T}{V}\right)\left(\frac{\partial V}{\partial T}\right)_P$ is 0.984, the molar volume is 76 $cm^3\ mol^{-1}$ and $C_P = 37.28\ JK^{-1}\ mol^{-1}$.

Soln. Substituting the given values in the expression

$$\mu_{JT} = \frac{V_m}{C_P}\left[\frac{T}{V}\left(\frac{\partial V}{\partial T}\right)_P - 1\right]$$

We get,
$$\mu_{JT} = \frac{\left(76\times10^{-6}\,m^3 mol^{-1}\right)}{\left(37.28 JK^{-1}mol^{-1}\right)}(0.984-1)$$

$$= -0.032\,6\times10^{-6}\,KJ^{-1}m^3 = -0.032\,6\times10^{-6}\,K\left(Pam^3\right)^{-1}m^3$$

$$= -0.032\,6\times10^{-6}\,K\left(1\ atm/101.325\times10^3\right)^{-1} = -0.003\,3\ K\ atm^{-1}$$

4. Show that inversion temperature, $T_i = \frac{1}{\alpha_i}$ for ideal gas.

Soln. $\mu_{J.T} = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]$

(If $T = T_i$) than $\mu_{J,T}$ becomes zero.

$$0 = \frac{1}{C_P}\left[T_i\left(\frac{\partial V}{\partial T}\right)_P - V\right] \Rightarrow T_i\left(\frac{\partial V}{\partial T}\right)_P = V$$

$$\Rightarrow \quad T_i = \frac{V}{\left(\frac{\partial V}{\partial T}\right)_P} = \frac{1}{\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P} = \frac{1}{\alpha_i}$$

$$\boxed{T_i = \frac{1}{\alpha_i}} \qquad \text{proved.}$$

Note: (1) Isothermal J.T. coefficient (ϕ)

$$(\phi) = \left(\frac{\partial H}{\partial P}\right)_T$$

(2) Isoenthalpic J.T. coefficient (μ)

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H \qquad \because \qquad \mu_{J.T} = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T \Rightarrow \boxed{\mu_{J.T} = \frac{1}{C_P}\phi}$$

Evaluation of $\left(\frac{\partial H}{\partial P}\right)_T$ from μ_{JT} of a van der Waals gas :

We know that, $\left(\frac{\partial H}{\partial P}\right)_T = -C_P \mu_{JT}$ ... (i)

And $\mu_{JT} = \frac{1}{C_P}\left(\frac{2a}{RT} - b\right)$ ... (ii)

From equation (i) and (ii), we get

$$\left(\frac{\partial H_m}{\partial P}\right)_T = b - \frac{2a}{RT}$$

For a gas undergoing isothermal expansion or compression, we will have

$$\Delta H_m = \left(b - \frac{2a}{RT}\right)\Delta P$$

Problem : Calculate the value of ΔH for the isothermal compression at 300K of 1 mol of nitrogen from 10^5 Pa to 500×10^5 Pa. Given: $a = 135.78$ $(dm^3)^2$ kPa mol^{-2} and $b = 0.039$ dm^3 mol^{-1}.

Soln. We have,

$$\Delta p = 500\times10^5\,Pa - 1\times10^5\,Pa = 499\times10^5\,Pa = 499\times10^2\,kPa$$

$$a = 135.78\left(dm^3\right)^2\,kPa\,mol^{-2}$$

$$b = 0.039\,dm^3 mol^{-1}$$

Substituting these values in the expression,

$$\Delta H_m = \left(b - \frac{2a}{RT}\right)\Delta p$$

We get, $\Delta H_m = \left[0.039 dm^3 mol^{-1} - \frac{2\times135.78\ dm^6 kPa\ mol^{-2}}{(8.314\ dm^3\ kPa\ K^{-1} mol^{-1})(300K)}\right](499\times10^2\ kPa)$

$= (0.039\ dm^3\ mol^{-1} - 0.108\ 9\ dm^3\ mol^{-1})(499\times10^2\ kPa)$

$= -3\ 488\ dm^3\ kPa\ mol^{-1} = -3.488\ kJ\ mol^{-1}$

Calculation of various thermodynamic relation for van der waal's relation:

1. Expression of W:

$dw = -p_{ext}.dv$

For reversible change in volume, $P_{ext} = P_{int} \pm dP \simeq P_{int}$

$\therefore \quad dw = -P_{int}\ dv \Rightarrow \int dw = -\int_{V_1}^{V_2}\left(\frac{nRT}{V-nb} - \frac{n^2a}{V^2}\right)dV$

$$\boxed{W = -nRT\ \ell n\frac{V_2-nb}{V_1-nb} - n^2a\left(\frac{1}{V_2} - \frac{1}{V_1}\right)}$$

2. Expressed for ΔU:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

For vander waal gas $\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V-nb}$

$$\therefore \quad \left(\frac{\partial U}{\partial V}\right)_T = \frac{nRT}{V-nb} - P = \frac{nRT}{(V-nb)} - \left(\frac{nRT}{(V-nb)} - \frac{n^2a}{V^2}\right) = \frac{n^2a}{V^2} \Rightarrow \left(\frac{\partial U}{\partial V}\right)_T = \frac{n^2a}{V^2}$$

$\because \quad U = f(T,V)$

$$\therefore \quad dU = \left(\frac{\partial U}{\partial V}\right)_V .dT + \left(\frac{\partial U}{\partial T}\right)_V .dV$$

For Isothermal change $dT = 0$

$$\therefore \quad dU = \left(\frac{\partial U}{\partial V}\right)_T .dV \Rightarrow \int dU = \int_{V_1}^{V_2}\frac{n^2a}{V^2}dV$$

$$\Rightarrow \quad \boxed{\Delta U = -n^2a\left(\frac{1}{V^2} - \frac{1}{V_1}\right)}$$

Similarly, $q = \Delta U - w$

$$\Rightarrow \quad \boxed{q = nRT\ell n\frac{V_2-nb}{V_1-nb}}$$

3. Expression for ΔH :

$$\because \quad \Delta H = \Delta U + \Delta(PV)$$

$$\Delta H = -n^2a\left(\frac{1}{V_2} - \frac{1}{V_1}\right) + \Delta\left[\left(\frac{nRT}{V-nb} - \frac{n^2a}{V^2}\right)V\right]$$

$$\Delta H = -n^2a\left(\frac{1}{V_2} - \frac{1}{V_1}\right) + nRT\left(\frac{V_2}{V_2-nb} - \frac{V_1}{V_1-nb}\right) - n^2a\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

$$\boxed{\Delta H = -2n^2a\left(\frac{1}{V_2} - \frac{1}{V_1}\right) + nRT\left(\frac{V_2}{(V_2-nb)} - \frac{V_1}{(V_1-nb)}\right)}$$

SOLVED PROBLEMS

1. When 229 J of energy is supplied to 3 moles of a gas at constant pressure, the temperature of the gas increased by 2.55 K. Calculate C_p and C_v for the gas, assuming ideal behaviour. **[GATE 1996]**

Soln. Given, $dq_p = 229$ J, n = 3 mole and dt = 2.55K

Since, we know that

$$dq_p = nC_P dt$$

$$229J = 3\ mol \times C_P \times 2.55K$$

$$C_P = \frac{229J}{3\ mol \times 2.55K}$$

$$\Rightarrow C_P = 29.9\ J\ mol^{-1}K^{-1}$$

Since, $C_P - C_V = R$ (for ideal behaviour)

$$29.9\ J\ mol^{-1}\ K^{-1} - C_V = 8.314\ J\ K^{-1}\ mol^{-1}$$

$$C_V = (29.9 - 8.314)\ JK^{-1}mol^{-1}$$

$$C_V = 21.58\ J\ K^{-1}mol^{-1}$$

2. One mole of an ideal gas $\left(C_P = 29.234\ JK^{-1}mol^{-1}\right)$ is expanded reversibly and adiabatically from 1 dm^3 to 10 dm^3. If the initial temperature is 750 K, the final temperature will be **[GATE 1996]**

(a) 1000K (b) 750 K (c) 300K (d) 100 K

Soln. Given, $T_1 = 750, V_1 = 1\ dm^3, V_2 = 10\ dm^3, T_2 = ?$ and $C_P = 29.234\ JK^{-1}mol^{-1}$

We know that, $C_P - C_V = R$

$$29.234\ JK^{-1}mol^{-1} - C_V = 8.314\ JK^{-1}mol^{-1}$$

$$C_V = 20.92\ JK^{-1}mol^{-1}$$

$$\therefore \quad \gamma = \frac{C_P}{C_V} = \frac{29.234\ JK^{-1}mol^{-1}}{20.92\ JK^{-1}mol^{-1}}$$

$$\gamma = 1.4$$

Since, $T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$

$$\frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{\gamma-1} \Rightarrow \frac{750K}{T_2} = \left(\frac{10}{1}\right)^{1.4-1} \Rightarrow \frac{750K}{T_2} = (10)^{0.4} \Rightarrow \frac{750K}{T_2} = 2.51$$

$$T_2 = \frac{750K}{2.51} = 300K$$

Correct option is (c).

3. The relationship between volume change in an isothermal process (ΔV_i) and an adiabatic process (ΔV_a) for a pressure change from P_1 to P_2 is **[GATE 1998]**

(a) $\Delta V_i > \Delta V_a$ (b) $\Delta V_i < \Delta V_a$ (c) $\Delta V_i = \Delta V_a$ (d) $\Delta V_i = \Delta V_a = 0$

Soln. Isothermal Process:

For isothermal process, we know that PV= constant

$\Rightarrow$ $P_1V_1 = P_2V_2;\ P_iV_i = P_fV_{iso}$

$\Rightarrow$ $\boxed{\frac{V_{iso}}{V_i} = \frac{P_i}{P_f}}$ ... (i)

Adiabatic Process:

For adiabatic process, we know that

PV^{γ} = constant

$\Rightarrow$ $P_1V_1^{\gamma} = P_2V_2^{\gamma};\ P_iV_i^{\gamma} = P_fV_{adia}^{\gamma};\ \left(\frac{V_{adia}}{V_i}\right)^{\gamma} = \frac{P_i}{P_f};\ \frac{V_{adia}}{V_i} = \left(\frac{P_i}{P_f}\right)^{\frac{1}{\gamma}}$ ... (ii)

From (i) & (ii), we have $\frac{V_{adia}}{V_i} = \left(\frac{V_{iso}}{V_i}\right)^{\frac{1}{\gamma}}$

Taking log on both the sides, we get

$$\log_{10}\left(\frac{V_{adia}}{V_i}\right) = \frac{1}{\gamma}\log_{10}\left(\frac{V_{iso}}{V_i}\right);\ \log_{10}\left(\frac{V_{iso}}{V_i}\right) = \gamma\log_{10}\left(\frac{V_{adia}}{V_i}\right) \quad \text{... (iii)}$$

Now since, $V_{iso} > V_i \Rightarrow \frac{V_{iso}}{V_i} > 1 \Rightarrow \log\left(\frac{V_{iso}}{V_i}\right) > 0$

And $V_{adia} > V_i \Rightarrow \frac{V_{adia}}{V_i} > 1 \Rightarrow \log\left(\frac{V_{adia}}{V_i}\right) > 0$

And $\boxed{\text{Also, } \gamma > 1}$

Therefore it is clear from the Equation (iii)

$$\log\left(\frac{V_{iso}}{V_i}\right) > \log\left(\frac{V_{adia}}{V_i}\right);\ \frac{V_{iso}}{V_i} > \frac{V_{adia}}{V_i}$$

$\Rightarrow$ $\boxed{V_{iso} > V_{adia}}$ $[\because V_i > 0]$

4. For an ideal gas following adiabatic reversible expansion, plot of log p versus log V is linear with a slope equal to $\left(\gamma = \frac{C_P}{C_V}\right)$ **[GATE 2000]**

(a) $\frac{1}{\gamma}$ (b) $-\frac{1}{\gamma}$ (c) γ (d) $-\gamma$

Soln. For adiabatic process, we know that

$$PV^{\gamma} = \text{constant} = k$$

$$P = kV^{-\gamma}$$

Taking log both side we get

$$\log P = \log k - \gamma \log V$$

Or, $\log P = -\gamma \log V + \log k$ ... (i)

Since, $y = mx + c$ ... (ii)

From equation (i) and (ii), we get

$$\text{slope} = m = \tan\theta = -\gamma$$

So, correct option is (a)

5. The internal pressure of one mole of a van der Waal gas is equal to **[GATE 1996]**

(a) zero (b) b^2 (c) $\frac{a}{v^2}$ (d) $b - \frac{a}{RT}$

Soln. For real gas; $\left(P + \frac{a}{V^2}\right)(V - b) = RT \Rightarrow P = \left[\left(\frac{RT}{V-b}\right) - \frac{a}{V^2}\right]$

$$\therefore \quad \pi_T = T\left(\frac{\partial}{\partial T}\frac{RT}{(V-b)}\right)_V - \underbrace{\left(\frac{\partial}{\partial T}\frac{a}{V^2}\right)_V}_{\Downarrow 0} - P = T\frac{R}{(V-b)}\left(\frac{\partial T}{\partial T}\right)_V - P$$

$$= \frac{RT}{(V-b)} - P = \left(P + \frac{a}{V^2}\right) - P \qquad \left[\because \left(P + \frac{a}{V^2}\right) = \frac{RT}{(V-b)}\right]$$

$$\boxed{\pi_T = \frac{a}{V^2}}$$

6. The internal pressure of a van der Waals gas is **[GATE 2003]**
(a) independent of the molar volume
(b) inversely proportional to square of the molar volume
(c) inversely proportional to square of the molar volume
(d) directly proportional to the molar volume.

Soln. Since internal pressure $\pi_T = \frac{a}{v^2}$

Internal pressure is inversely proportional to square of the molar volume

Correct option is (c)

7. In an adiabatic system, the work done to change its state from A to B is **[GATE 2005]**
(a) dependent on path from A to B
(b) independent of path from A to B
(c) path dependence is related to particulars of states A and B
(d) path dependence is related to both states A and B and choice of path.

Soln. **Correct option is (b)**

8. The internal pressure, $\pi_T = T\left(\frac{\partial P}{\partial T}\right)_v - p$ for one mole a vander Waals gas is **[GATE 2005]**

(a) $\frac{a}{V^2}$ (b) $\frac{a}{V^2}\left(\frac{RT}{V-b}\right)$ (c) zero (d) $\frac{RT}{V-b}$

Soln. For vander Waal gas, for one mole,

$$\left(P+\frac{a}{V^2}\right)(V-b)=RT$$

$$P=\frac{RT}{(V-b)}-\frac{a}{V^2} \quad \ldots (i)$$

$$\Rightarrow \quad \left(\frac{\partial P}{\partial T}\right)_V=\frac{R}{V-b}$$

Since, given internal pressure, $\pi_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \Rightarrow \pi_T = T\frac{R}{(V-b)} - P$

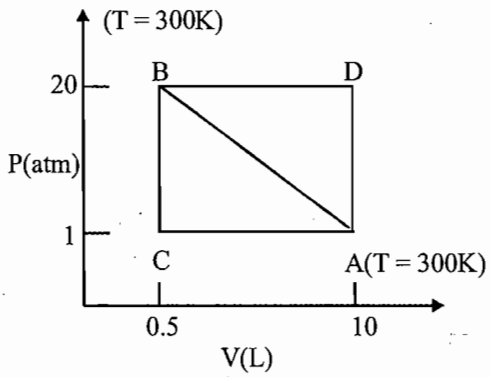
From (i), $\pi_T = p+\frac{a}{V^2} - p$

$$\therefore \quad \pi_T = \frac{a}{V^2}$$

Correct option is (a)

Common Data for Q. 9 and Q. 10. **[GATE 2006]**

Consider the following P-V diagram for an ideal gas that follows the diagonal path from A to B.



9. The work done (in atm-L) on the gas in the process is

(a) 9.5 (b) 99.75 (c) 190 (d) 10 ln (20)

Soln. Since, $w = -nRT\ln\frac{V_2}{V_1} = -P_1V_1\ln\frac{V_2}{V_1} = -P_2V_2\ln\frac{V_2}{V_1}$

$$w = -10\ln\frac{0.5}{10} = 10\ln(20)$$

Correct option is (d)

10. For the above process,

(a) $\Delta H = W$ (b) $\Delta H = Q$ (c) $\Delta H = \Delta G$ (d) $\Delta H = \Delta E$

Soln. $\Delta H = (pdT) = 0$

$\Delta E = C_v dT = 0$

$\Delta H = \Delta E$

Correct option is (d)

11. If a gas obeys the equation of state $P(V-nb)=nRT$, the ratio $\frac{(C_P-C_V)}{(C_P-C_V)_{ideal}}$ is: **[GATE 2008]**

(a) >1 (b) <1 (c) 1 (d) (1–b)

Soln. Given, $P(V-nb)=nRT$ ... (i)

$$P=\frac{nRT}{V-nb}$$

$$\left(\frac{\partial P}{\partial T}\right)_V=\left(\frac{nR}{V-nb}\right) \text{ and } pV-pnb=nRT$$

$$pV=nRT+pnb \Rightarrow V=\frac{nRT}{p}+nb$$

$$\left(\frac{\partial V}{\partial T}\right)_P=\frac{nR}{P} \quad \text{... (ii)}$$

$\because$ $C_P-C_V=T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P$

Or, $C_P-C_V=T\times\left(\frac{nR}{V-nb}\right)\times\frac{nR}{P}=nR$ (from (i))

we know that, $(C_P-C_V)_{ideal}=nR$

$\therefore$ $\frac{C_P-C_V}{(C_P-C_V)_{ideal}}=\frac{nR}{nR} \Rightarrow \frac{C_P-C_V}{(C_P-C_V)_{ideal}}=1$

Correct option is (c)

12. Show that $C_V=\frac{R}{\gamma-1}$ and $C_P=\left(\frac{\gamma}{\gamma-1}\right)R$

Soln. $C_P-C_V=R \Rightarrow \frac{C_P}{C_V}-1=\frac{R}{C_V} \Rightarrow \gamma-1=\frac{R}{C_V}$

$\therefore$ $C_V=\left(\frac{R}{\gamma-1}\right)$

Again, $C_P-\frac{R}{\gamma-1}=R$

$\Rightarrow$ $C_P=R+\frac{R}{\gamma-1}=R\left(1+\frac{1}{\gamma-1}\right)=R\left(\frac{\gamma-1+1}{\gamma-1}\right)$

$$\boxed{C_P=R\left(\frac{\gamma}{\gamma-1}\right)}$$

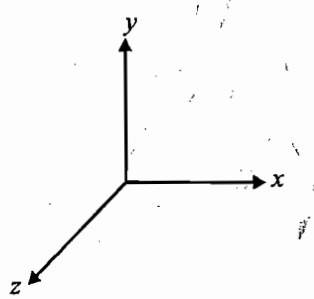
Proved.

Degree of Freedom:

The degree of freedom of a molecule are defined as the independent number of parameters required to describe the state of the molecule completely. The motion of atom and molecules is generally described in term of degree of freedom they possess. When a gaseous molecule is heated then the energy supplied to it may bring about three kind of motion in it (translational motion, rotational motion and vibrational motion).

It is the number of independent variables coordinates required to specify a molecule in the space or it is the kind of energies sustained by a molecule or by knowing the value of which we can predict about the kind of motion (viz translational, rotational and vibrational) executed by a molecule.

Both kind of molecules (linear and non linear) show three kinds of translational motion (i.e along x, y & z axes).



Non-linear molecules (like NO_2, SO_2, SO_3, CH_4 etc) show three kinds of Rotational motion

Linear molecules (like CO, CO_2, N_2, O_2 etc) show two kinds of rotational motion.

If there are N number of atoms, then the total degree of freedom (DOF) in the space = 3N i.e. Translational degree of freedom + rotational degree of freedom + vibrational degree of freedom= 3N

$$\Rightarrow \quad \boxed{N_{tr} + N_{rot} + N_{Vib} = 3N} \qquad \ldots (1)$$

For both kind of molecules (i.e linear and non-linear)

$N_{tr} = 3$

from equation (1)

$$\Rightarrow \quad 3 + N_{rot} + N_{Vib} = 3N$$

$$\Rightarrow \quad \boxed{N_{Vib} = 3N - (3 + N_{rot})} \qquad \ldots (2)$$

For Linear Molecule: $N_{rot} = 2$

from equation (2)

$$\Rightarrow \quad N_{Vib} = 3N - (3 + 2)$$

$$\Rightarrow \quad \boxed{N_{Vib} = 3N - 5}$$

For non-linear molecular: $N_{rot} = 3$

from equation (2)

$$\Rightarrow \quad N_{Vib} = 3N - (3 + 3)$$

$$\Rightarrow \quad \boxed{N_{Vib} = 3N - 6}$$

Problem-1. Calculate N_{Vib} for the following moleculers NO_2, SO_2, CO, SO_3, CO_2, CH_4, N_2, O_2,

Soln. Here linear molcules are CO, CO_2, N_2, O_2.

For these molecule $\boxed{N_{Vib} = 3N - 5}$

(i) CO

Here N = 2 $\therefore N_{Vib} = 3\times2-5 = 1$

(ii) CO_2

Here N = 3 $\therefore N_{Vib} = 3\times3-5 = 4$

(iii) N_2

Here N = 2 $\therefore N_{Vib} = 3\times2-5 = 1$

(iv) O_2

Here N = 2 $\therefore N_{Vib} = 3\times2-5 = 1$

And non-linear moleculers are

NO_2, SO_2, SO_3, CH_4,

For these non-linear moleculers.

N_{Vib} is given as $N_{Vib} = 3N-6$

(i) NO_2

Here N = 3 $\therefore N_{Vib} = 3\times3-6 = 3$

(ii) SO_2

Here N = 3 $\therefore N_{Vib} = 3\times3-6 = 3$

(iii) SO_3

Here N = 4 $\therefore N_{Vib} = 3\times4-6 = 6$

(iv) CH_4 Here N = 5 $\therefore N_{Vib} = 3\times5-6 = 9$

Relation between C_V and Degree of Freedom(f):

If the degree of freedom of one molecule is f, then the degree of freedom of N molecules will be Nf.

Now from the equipartition theorem of energy, Average internal energy per degree of feedom per molecule is given as, $E = \frac{1}{2}kT$ (Where, k = Boltzman constant)

$$\Rightarrow \quad k = \frac{R}{N} = \frac{8.314\ J/Kmol}{6.023\times10^{23}\ mol^{-1}} \Rightarrow k = 1.38\times10^{-23}\ J\ K^{-1}$$

Average internal energy of all kind of molecules (i.e of N molecules)

$$E = \frac{1}{2}\,N f k T \Rightarrow E = \frac{1}{2}\,R f T$$

Now we know that

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_v \Rightarrow C_V = \left(\frac{\partial E}{\partial T}\right)_v$$

$$\Rightarrow \quad C_V = \left[\frac{\partial}{\partial T}\left(\frac{1}{2}R f T\right)\right]_v \Rightarrow C_V = \frac{1}{2}Rf\left(\frac{\partial T}{\partial T}\right)_v$$

$$\Rightarrow \quad C_V = \frac{1}{2}Rf\times1 \Rightarrow \boxed{C_V = \frac{Rf}{2}}$$

According to the principle of equipartition of energy

Degree of freedom	Symbol	Contribution to C_V
Translational	N_{tr}	$\frac{R}{2}$
Rotational	N_{rot}	$\frac{R}{2}$
Vibrational	N_{Vib}	R, at high temperature 0.2R, at room temperature 0, at very low temperature

i.e. at room temperature the contribution to C_V from N_{vib} is only 20% then we get

$\therefore$ Contribution to C_V from N_{Vib} $= R \times \frac{20}{100} = 0.2\ R$

At high temperature,

$$\boxed{(C_V)_{total} = N_{tr}\left(\frac{R}{2}\right) + N_{rot}\left(\frac{R}{2}\right) + N_{Vib}(R)}$$

At room temperature,

$$\boxed{(C_V)_{total} = N_{tr}\left(\frac{R}{2}\right) + N_{rot}\left(\frac{R}{2}\right) + N_{Vib}(0.20R)}$$

Problem-2. Estimate γ at room temperature for (a) He, (b) CH_4
Assuming these gases as ideal gases. What will be the value of γ at higher temperature?

Soln : Case-I: At room temperature

(a) He Helium consists of one atom only and atoms have only translation motion.

$\therefore$ $N_{tr} = 3,\ N_{rot} = 0,\ N_{Vib} = 0$

$\therefore$ $(C_V)_{total} = N_{tr}\left(\frac{R}{2}\right) + N_{rot}\left(\frac{R}{2}\right) + N_{vib}\ (0.20R)$

$(C_V)_{total} = 3 \times \frac{R}{2} + 0 + 0 \quad \Rightarrow C_V = \frac{3R}{2}$

And $C_P = C_V + R = \frac{3}{2}R + R = \frac{5}{2}R$

$\therefore$ $\gamma = \frac{C_P}{C_V} = \frac{(5/2)R}{(3/2)R} = \frac{5}{3} = 1.66$

(b) CH_4 it is a non linear molecule

Here $N_{tr} = 3,\ N_{rot} = 3$ and $N = 5$

$\therefore$ $N_{vib} = 3N - 6 \Rightarrow N_{vib} = 3 \times 5 - 6 \Rightarrow N_{vib} = 9$

$\therefore$ $$\boxed{(C_V) = N_{tr}\left(\frac{R}{2}\right) + N_{rot}\left(\frac{R}{2}\right) + N_{Vib}(0.20R)}$$

$\Rightarrow$ $C_V = 3\frac{R}{2} + \frac{3R}{2} + 9 \times 0.20\ R \Rightarrow C_V = 3\ R + 1.80\ R \Rightarrow C_V = 4.80\ R$

$\Rightarrow \quad C_V = 4.80 \times 8.314 \frac{J}{K\,mol} = 39.9072\ J/K.\ mol$

$\therefore \quad C_P = C_V + R = (39.90 + 8.3140) = 48.22\ J/K$

$\Rightarrow \quad \gamma = \frac{C_P}{C_V} = \frac{48.22}{39.90} = 1.20$

Or $\quad C_P = C_V + R = 4.80\,R + R = 5.80\,R$

$\therefore \quad \gamma = \frac{C_P}{C_V} = \frac{5.80R}{4.80R} = 1.20$ Ans

Case-II: At high temperature:

(a) **He :** Same Value

Helium consists of atom only and atoms have only translation motion

$\therefore \quad N_{tr} = 3,\ N_{rot} = 0$ and $N_{vib} = 0$

$\therefore \quad (C_V)_{total} = N_{tr}\left(\frac{R}{2}\right) + N_{rot}\left(\frac{R}{2}\right) + N_{vib}(R)$

$\Rightarrow \quad C_V = 3 \times \frac{R}{2} + 0 + 0 \Rightarrow C_V = \frac{3R}{2}$

$\Rightarrow \quad C_V = C_V + R = \frac{3}{2}R + R = \frac{5}{2}R$

$\therefore \quad \gamma = \frac{C_P}{C_V} = \frac{(5/2)R}{(3/2)R} = \frac{5}{3} = 1.66$

(b) CH_4 It is a non-linear molecule

Here $N_{tr} = 3,\ N_{rot} = 3,\ N = 5$

$\therefore \quad N_{vib} = 3N - 6 = 3 \times 5 - 6 \Rightarrow N_{vib} = 9$

$\therefore \quad (C_V)_{total} = N_{tr}\left(\frac{R}{2}\right) + N_{rot}\left(\frac{R}{2}\right) + N_{vib}(R)$

$\Rightarrow \quad C_V = \frac{3R}{2} + \frac{3R}{2} + 9 \Rightarrow R\,C_V = 3R + 9R \Rightarrow C_V = 12\,R$

$\therefore \quad C_P = C_V + R = 12\,R + R = 13\,R$

$\therefore \quad \gamma = \frac{C_P}{C_V} = \frac{13\,R}{12\,R} = 1.08$

On the basis of this question, we can say that on increasing temp C_P, C_V increases, but γ decreases.

PRACTICE SET

1. Adiabatic reversible expansion of a monoatomic gas (M) and a diatomic gas (D) at an initial temperature T_i, has been carried out independently from initial volume V_1 to final volume V_2. The final temperature (T_M for monoatomic and T_D for diatomic) attained will be **[GATE 2003]**

(a) $T_M = T_D > T_i$ (b) $T_M < T_D < T_i$ (c) $T_M > T_D > T_i$ (d) $T_M = T_D = T_i$

2. For one mole of an ideal gas $\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial V}{\partial P}\right)_T =$ **[GATE 2004]**

(a) -1 (b) $-\frac{R^2}{P^2}$ (c) $+1$ (d) $\frac{R^2}{P^2}$

3. One mole of an ideal gas $(C_V = 1.5\,R)$ at a temperature 500 K is compressed from 1.0 atm to 2.0 atm by a reversible isothermal path. Subsequently, it is expanded back to 1.0 atm by a reversible adiabatic path. The volume of the final state in litre is: **[GATE 2004]**

(a) 15.6 (b) 20.5 (c) 31.1 (d) 41.0

4. For an ideal gas $\left(\frac{\partial H}{\partial T}\right)_P =$

(a) C_V (b) C_P (c) 0 (d) 1

5. The vanderwaal equation is given by

$$\left(P + \frac{n^2 a}{v^2}\right)(v - nb) = nRT$$

The ratio $\frac{a}{b}$ has a dimension of

(a) atm/litre (b) litre atm/mole (c) litre/mole (d) litre atm $mole^{-2}$.

6. For a reverrisible adiabatic compression which realationship is true:

(a) $P_2^{1-\gamma}\, T_2^{1-\gamma} = P_1^{1-\gamma}\, T_1^{1-\gamma}$ (b) $P_2^{1-\gamma}\, T_1^{-\gamma} = P_1^{1-\gamma}\, T_2^{-\gamma}$

(c) $P_2^{1-\gamma}\, T_2^{-\gamma} = P_1^{1-\gamma}\, T_1^{\gamma}$ (d) $P_1 T_1^{\gamma} = P_2 T_2^{\gamma}$

7. For reversible adiabatic expansion of an ideal gas

$$T = \text{constant} \times P^x$$

The value of 'x' is:

(a) γ (b) $1 - \frac{1}{\gamma}$ (c) $\frac{1}{\gamma} - 1$ (d) $1 - \gamma$

8. Among W (work), Q (heat), U (internal energy) and S (entropy)

(a) W and U are path functions but Q and S are state functions
(b) W and S are path functions but Q and U are state functions.
(c) S and U are path functions but Q and W are state functions.
(d) W and Q are path functions but U and S are state functions.

9. Work (w) involved in isothermal reversible expansion from V_i to V_f of n moles of an ideal gas is

(a) $w = -nRT\ln(V_f / V_i)$ (b) $w = nRT\ln(V_f / V_i)$ **[NET Dec. 2013]**

(c) $w = -nRT(V_f / V_i)$ (d) $w = -nRT\log(V_f / V_i)$

10. The heat capacity of 10 mol of an ideal gas at a certain temperature is 300 JK^{-1} at constant pressure. The heat capacity of the same gas at the same temperature and at constant volume would be **[NET Dec. 2013]**

(a) 383 JK^{-1} (b) 217 JK^{-1} (c) 134 JK^{-1} (d) 466 JK^{-1}

11. At 300 K 2 moles of an ideal gas expand reversibly and isothermally from 1L to 10L. What is the entropy change for the process? $(R = 2 \text{ cal } K^{-1}mol^{-1}$ and in 10=2.303)

(a) 9.2 cal K^{-1} mol^{-1} (b) 4.6 cal K^{-1} mol^{-1}

(c) 2.76 cal K^{-1} mol^{-1} (d) 0

12. Consider the following statement :

1. The Boyle temperature for a vander waal gas is $T_B = \frac{a}{2Rb}$
2. The inversion temperature is given by equation $T_i = \frac{2a}{Rb}$
3. The Joule-Thomson coefficient for an ideal gas is zero.
4. H_2 and He show cooling at ordinary temperature of these.

The correct statement is:

(a) 1, 4 (b) 2, 3 (c) 1, 2, 3 (d) 2, 3, 4

13. Work done in a free expansion process is

(a) zero (b) minimum

(c) maximum (d) positive

14. A gas is expanded adiabatically from 750 K to its twice volume than the final volume is if $(C_P = \frac{5}{2}R)$, final temperature is:

(a) 100 (b) 300 (c) 475 (d) 750

15. An ideal gas expands by following an equation PV^a = constant. In which case does one expect heating?

(a) $3 > a > 2$ (b) $2 > a > 1$ (c) $0 < a < 1$ (d) $-1 < a < 0$ **[NET June 2011]**

16. The ΔS for 3 mole of an ideal gas (diatomic) which is heated and compressed from 298K and 1 bar to 398K and 5 bar $\left(C_P = \frac{7}{2}R\right)$

(a) –14.88 J/K (b) 14.88 J/K

(c) –4.62 J/K (d) 4.62 J/K

17. The C_P/C_V ratio of a gas mixture consisting of 8 g of helium and 16 g of oxygen is:

(a) 1.33 (b) 1.47 (c) 1.59 (d) 2

18. Consider the following statement

(1) The value of $\frac{C_P}{C_P + C_V}$ for helium is $\frac{8}{3}\left(\gamma = \frac{5}{3}\right)$ (2) The value of $\frac{C_P - C_V}{C_P + C_V}$ for H_2 is $\frac{1}{6}\left(\gamma = \frac{7}{5}\right)$

Which of the following statement is correct.

(a) 1 only (b) 2 only (c) both 1 and 2 (d) neither 1 nor 2

19. If an ideal gas having internal energy $U = \frac{1}{3}PV$ is expanded reversible and adiabatically from P_1, V_1, T_1 to P_2, V_2, T_2 then

(a) $TV^{-1/3} = \text{constant}$ (b) $TV^{1/3} = \text{constant}$

(c) $PV^{-1/3} = \text{constant}$ (d) $PV^{1/3} = \text{constant}$

20. One mole of an monoatomic gas $(\gamma = 1.66)$ is mixed with one mole of diatomic gas $(\gamma = 1.40)$. The value of γ for the mixture is:

(a) 1.40 (b) 1.50 (c) 1.53 (d) 3.07

ANSWER KEY					
Questions	1	2	3	4	5
Option	(b)	(d)	(c)	(b)	(b)
Questions	6	7	8	9	10
Option	(b)	(b)	(d)	(a)	(b)
Questions	11	12	13	14	15
Option	(b)	(b)	(a)	(c)	(c)
Questions	16	17	18	19	20
Option	(a)	(c)	(b)	(a)	(b)

Chapter 3

Second Law of Thermodynamics

Introduction:

The second law helps us to determine the direction in which energy can be transferred. It also helps us to predict whether a given process or a chemical reaction can occur spontaneously. It introduces a new concept of entropy. It also helps us to know the equilibrium conditions.

Statement of the Second Law of Thermodynamics :

1. "Heat cannot spontaneously pass from a colder to a warmer body." (**R.J.E calusius**).
2. "In an adiabatic process the entropy either increases or remains unchanged.

$$\Delta S \geq 0$$

where the sign (>) referes to the irreversible, the "equal" refers to the reversible case. (**P.S. Epstein**).

3. ***"Work can always be completely converted into heat but heat can't be completely converted into work without leaving a permanent change in the system or surroundings. Only a fraction of heat can be converted into useful work & the rest remains unavailable & unconverted.*** **[CSIR-NET]**
4. "In any irreversible process the total entropy of all bodies concerned is increased." (**G.N. Lewis**)
5. "The entropy function of a system of bodies tends to increase in all physical and chemical processes occurring in nature, if we include in the system all such bodies which are affected by the change." (**Saha**)

Carnot cycle or Carnot reversible heat engine:

The carnot cycle is a hypothetical, ideal & reversible cyclic process, devised by a french engineer Sadi Carnot (1824), to demonstrate the maximum convertibility of heat into work. An ideal machine to demonstrate this cycle is called carnot heat engine.

The work done in a carnot cycle is maximum because the various steps involved are reversible & the reversible work is the maximum possible work which a system can do.

Carnot heat engine is ideal and regarded as standard (ideal) by which the performance of an actual heat engine is compared.

Schematic plan:

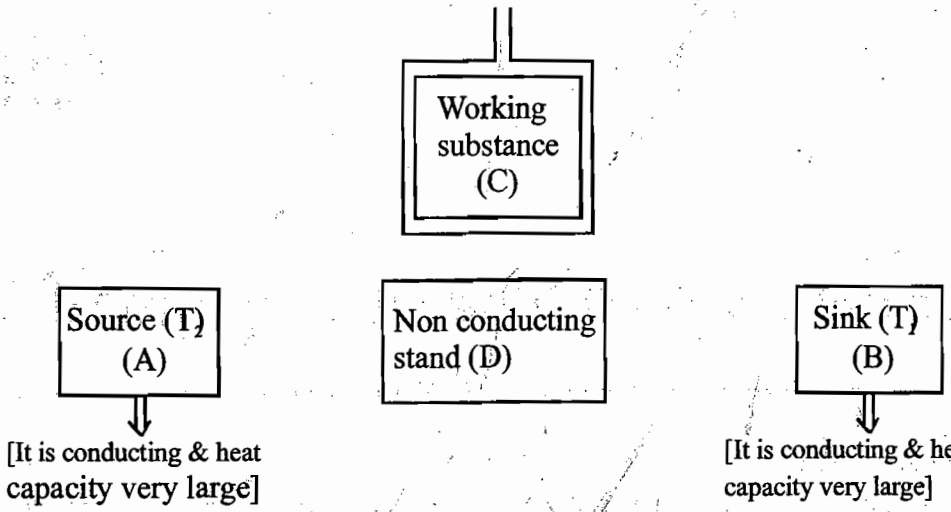
It consist of

(i) Source of heat (A), at high temperature T_2.

(ii) Sink (B) , at lower temperature T_1

(iii) Working substance (C)

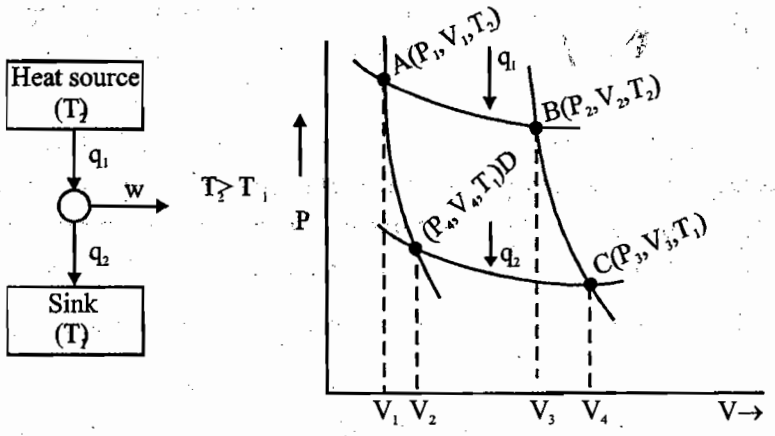
(iv) Perfect heat insulating stand (D)


Working substance (C)
Source (T2) (A)
[It is conducting & heat capacity very large]
Non conducting stand (D)
Sink (T1) (B)
[It is conducting & heat capacity very large]

The ideal carnot's cycle is the cycle in which working substance is an ideal gas.

Operations involved in Carnot cycle:

This cycle involves four operations. These are as follows.



Indicator Diagram of Carnot Cycle

Step 1: Isothermal and reversible expansion of working substance:

Cyclinder is placed on the source, load on the piston is decreased, working substance expands, external work happens. Fall in temperature, but it is in the contact with the source, Thus maintains the temperature quantity of heat absorbed is q_1.

$$T_2 = \text{constant}. \qquad \therefore \qquad \Delta U = 0$$

First law, $q_1 = -w_1 = RT_2 \ell n \frac{V_2}{V_1}$ ... (1)

Step 2: Adiabatic reversible expansion of working substance:

Cylinder is removed from the source put on the perfectly insulating pad. Load is further decreased to cause expansion of working substance adiabatically.

$\therefore \quad q = 0$ (From first law)

$$w_2 = \Delta U = C_V (T_1 - T_2) \qquad \text{... (2)}$$

Step 3: Isothermal and reversible compression of substance:

Cylinder is again transfer to the sink at temperature (T_1), load on the piston is slowly increased. Gas is compressed. Heat developed passes into the sink. Temperature remain constant at T_1.

$$q_2 = -w_3 = RT_1 \ell n \frac{V_4}{V_3} \qquad \text{... (3)}$$

Step 4: Adiabatic reversible compression of substance:

Cylinder is again transfer to the insulating pad. Load on the piston is again slightly increased, so that substance undergo slow adiabatic compression. Temperature rises from $T_1 \rightarrow T_2$

$$w_4 = C_v(T_2 - T_1) \quad \ldots(4)$$

Thus net work during one complete cycle.

$$W_{Total} = w_1 + w_2 + w_3 + w_4$$

$$= -RT_2 \ell n \frac{V_2}{V_1} + C_v(T_1 - T_2) - RT_1 \ell n \frac{V_4}{V_3} + C_v(T_2 - T_1)$$

But $C_v(T_1 - T_2) = -C_v(T_2 - T_1)$

$$\therefore \quad \boxed{W_{Total} = -RT_2 \ell n \frac{V_2}{V_1} - RT_1 \ell n \frac{V_4}{V_3}} \quad \ldots(5)$$

Now for adiabatic curve BC and DA

$$TV^{\gamma-1} = \text{Constant}$$

for curve BC, $T_2V_2^{\gamma-1} = T_1V_3^{\gamma-1}$

$$\therefore \quad \frac{T_1}{T_2} = \left(\frac{V_2}{V_3}\right)^{\gamma-1} \quad \ldots(6)$$

for curve DA, $T_1V_4^{\gamma-1} = T_2V_1^{\gamma-1}$

$$\therefore \quad \frac{T_1}{T_2} = \left(\frac{V_1}{V_4}\right)^{\gamma-1} \quad \ldots(7)$$

from equation (6) and (7)

$$\left(\frac{V_2}{V_3}\right)^{\gamma-1} = \left(\frac{V_1}{V_4}\right)^{\gamma-1}$$

$$\therefore \quad \boxed{\frac{V_2}{V_1} = \frac{V_3}{V_4}} \quad \ldots(8)$$

Putting value of equation (8) in equation (5)

$$W_{Total} = -RT_2 \ell n \frac{V_2}{V_1} - RT_1 \ell n \frac{V_1}{V_2} = -RT_2 \ell n \frac{V_2}{V_1} + RT_1 \ell n \frac{V_2}{V_1}$$

$$\boxed{W_{Total} = -R \ell n \frac{V_2}{V_1}(T_2 - T_1)} \quad \ldots(9)$$

Efficiency (η) of carnot heat engine:

The ratio of work done by the system to the amount of heat transferred to the system at the higher temperature.

$$\eta = \frac{-W_{Total}}{q_2} = \frac{q_2 + q_1}{q_2} = 1 + \frac{q_1}{q_2}$$

Absorbed heat $q_1 = RT_2 \ell n \frac{V_2}{V_1}$

$$\therefore \quad \eta = \frac{-w}{q_1} = \frac{-\left[-R \ell n \frac{V_2}{V_1}(T_2 - T_1)\right]}{RT_2 \ell n \frac{V_2}{V_1}}$$

$$\Rightarrow \quad \boxed{\eta = 1 - \frac{T_1}{T_2}} \qquad \ldots (10)$$

Discussion of above equation (10):

(i) η does not depend on the working substance used.

(ii) η depends only on the ratio of sink to source temperature

(iii) η is always less than one.

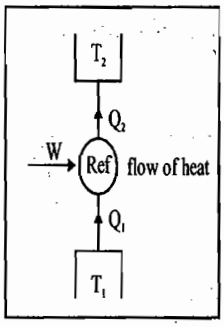
(iv) η is one only when $\frac{T_1}{T_2}$ is zero. i.e. when $T_1 = 0K\,(-273°C)$ or $T_2 = \infty$. Both these temp. are impossible to obtain. Therefore, it is impossible to construct a heat engine whose efficiency is unity or 100%. That is heat can't be transformed completely into work.

(v) For all reversible cycle operating between the same initial and final temperature, the efficiency is the same.

Refrigerator:

Energy will not flow spontaneously from a low temperature to a high temperature without any work. Refrigerator does this work. Refrigerator is a machine operates in a manner opposite to that of a heat engine. (Working substance take heat from the low temp. source then same work is performed on it & finally it rejects heat to a high temperature source. Space to the refrigerated is the low temp. source & surrounding atmosphere is high temperature source.

In carnot engine heat is input work is output. In refrigerator heat is output & work is input.



Comparison of efficiencies of reversible and irreversible cyclic processes.

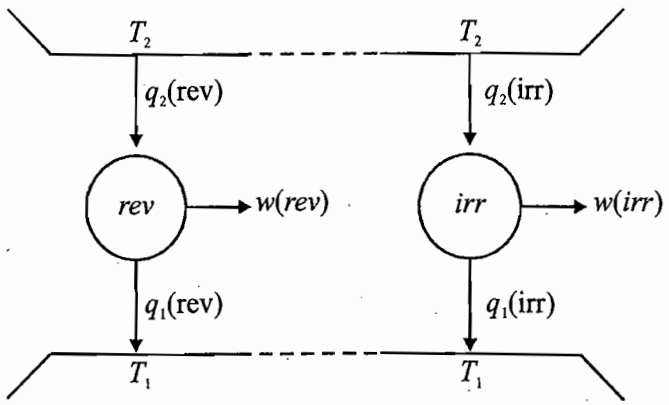
The efficiency of a reversible Carnot cycle is the theoretically possible maximum value which an engine can have. Since the various processes of this type of engine are to be carried out reversibly, therefore, such type of an engine does not have any realistic basis because reversible processes are idealized concepts which can never be realized. A real heat engine, which is irreversible in nature, will have efficiency smaller than the reversible heat engine.

Let us have two cycles, one operating reversibly and the other irreversibly. Let both of them operate between the same two temperature T_1 and T_2 and involve ideal gas as the working substance. These two cycles along with q values, are shown in the figure below.

(A) Isothermal expansion form volume V_1 to V_2. The expressions for the work involved are

$$-w_2(rev) = q_2(rev) = RT_2 \ln \frac{V_2}{V_1}$$

And $$-w_2(irr) = q_2(irr) = p_{opp}(V_2 - V_1)$$



Since we known that $|w_2(rev)| > |w_2(irr)|$, therefore,

$$q_2(rev) > q_2(irr)$$

(B) Isothermal compression from volume V_3 to V_4. The expressions for the work involved are

$$-w_1(rev) = q_1(rev) = RT_1 \ln \frac{V_4}{V_3}$$

$$-w_1(irr) = q_1(irr) = p'_{opp}(V_4 - V_3)$$

Now since in the irreversible process, more work is done as compared to that in the reversible process, we have

$$w_1(irr) > w_1(rev)$$

It follows that

$$|q_1(irr)| > |q_1(rev)| \text{ or } |q_1(rev)| < |q_1(irr)|$$

Now the efficiencies of the two cycles are

$$\eta(rev) = \frac{q_2(rev) + q_1(rev)}{q_2(rev)} = \frac{q_2(rev) - |q_1(rev)|}{q_2(rev)} = 1 - \frac{|q_1(rev)|}{q_2(rev)}$$

$$\eta(irr) = \frac{q_2(irr) + q_1(irr)}{q_2(irr)} = \frac{q_2(irr) - |q_1(irr)|}{q_2(irr)} = 1 - \frac{|q_1(irr)|}{q_2(irr)}$$

Now since $q_2(rev) > q_2(irr)$ and $|q_1(rev)| < |q_1(irr)|$, therefore, it follows that

$$\frac{|q_1(rev)|}{q_2(rev)} < \frac{|q_1(irr)|}{q_2(irr)} \text{ or } \left\{1 - \frac{|q_1(rev)|}{q_2(rev)}\right\} > \left\{1 - \frac{|q_1(irr)|}{q_2(irr)}\right\}$$

i.e. $\eta(rev) > \eta(irr)$

Basic Conclusion from Efficiency of a Carnot Cycle :

For a reversible Carnot cycle operating between two temperatures T_2 and T_1, the efficiency is given as

$$\eta = \frac{q_2 + q_1}{q_2} = \frac{T_2 - T_1}{T_2}$$

where q_2 and q_1 are the heats exchanged with the thermal reservoirs at temperatures T_2 and T_1, respectively. Rewriting the above expression, we have

Or, $$1 + \frac{q_1}{q_2} = 1 - \frac{T_1}{T_2} \text{ or } \frac{q_1}{q_2} = -\frac{T_1}{T_2}$$

Or, $$\frac{q_2}{T_2} + \frac{q_1}{T_1} = 0$$

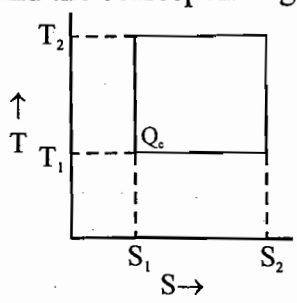
that is, the sum of the ratios of the heat involved and the corresponding temperature is zero for a Carnot cycle.

T—S diagram of carnot cycle:

Total heat taken by system $dQ = TdS$

$$Q = T_2(S_2 - S_1)$$

Heat energy converted into work

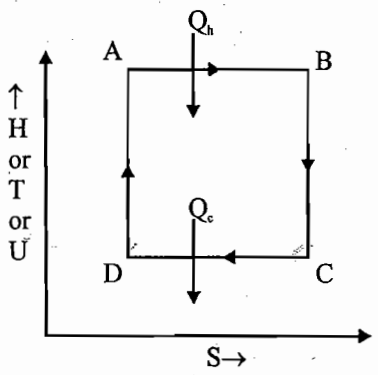


$$-w = dQ = (T_2 - T_1)(S_2 - S_1)$$

$$\therefore \quad \eta = \frac{-w}{Q} = \frac{(T_2 - T_1)(S_2 - S_1)}{T_2(S_2 - S_1)} = \frac{T_2 - T_1}{T_2}$$

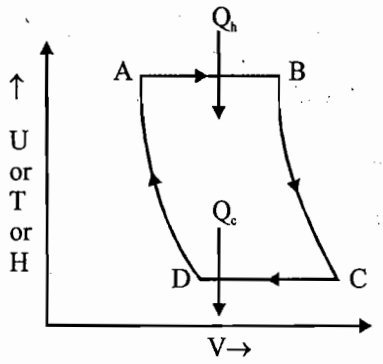
$$\Rightarrow \quad \boxed{\eta = 1 - \frac{T_1}{T_2}}$$

H vs S or T Vs S or U vs S diagram for carnot's engine.



AB = reversible isothermal expansion
BC = reversible adiabatic expansion
CD = reversible isothermal compression
DA = reversible adiabatic compression

U vs V or T vs V or H vs V diagram for carnot's engine:



AB = reversible isothermal expansion
BC = reversible adiabatic expansion
CD = reversible isothermal compression
DA = reversible adiabatic compression

Coefficient of performance (β):

The ratio of heat transferred from a lower temperature to a higher temperature to the work done on the machine to cause this removal, i.e. $\beta = \frac{|q_C|}{w}$

The less the work done the more efficient the operation and greater the coefficient of performance.

$\because \quad w_{irr} > w_{rev}, \quad \therefore \quad \beta_{rev} > \beta_{irr}$

$$\beta = \frac{|q_C|}{|q_h| - |q_C|} = \frac{T_1}{T_2 - T_1}$$

At $T_1 \to 0$ kelvin $\quad \beta = 0$

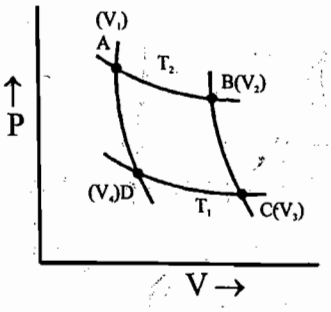
$$\therefore \quad w = \frac{|q_C|}{\beta} = \frac{(q_C)}{0} = \infty$$

Thus as the temperature of a system is lowered the amount of work required to lower the temperature further increases rapidly and approaches infinity as the zero kelvin temperature is attained.

Efficiency in the form of expansion ration (ρ)/Adiabatic expansion ratio:

$$\boxed{\rho = \frac{V_3}{V_2} = \frac{V_4}{V_1}}$$

Efficiency $(\eta) = 1 - \frac{T_1}{T_2}$



For adiabatic curve $TV^{\gamma-1}$

$\therefore \quad T_2 V_2^{(\gamma-1)} = T_1 V_3^{(\gamma-1)}$

$$\frac{T_1}{T_2} = \left(\frac{V_2}{V_3}\right)^{\gamma-1} \Rightarrow \frac{T_1}{T_2} = \frac{1}{\left(\frac{V_2}{V_3}\right)^{\gamma-1}} = \frac{1}{(\rho)^{\gamma-1}}$$

$\therefore \quad \boxed{\eta = 1 - \left(\frac{1}{\rho}\right)^{\gamma-1}}$

Relation between (η) and (β):

$\because \quad \beta = \frac{T_1}{T_2 - T_1} \qquad T_2 > T_1$

Again. $\eta = \frac{T_2 - T_1}{T_2} \Rightarrow \frac{1}{\eta} = \frac{T_2}{T_2 - T_1} \Rightarrow \frac{1}{\eta} - 1 = \frac{T_2}{T_2 - T_1} - 1 \Rightarrow \frac{1-\eta}{\eta} = \frac{T_2 - T_2 + 1}{T_2 - T_1} = \frac{T_1}{T_2 - T_1}$

$$\boxed{\beta = \frac{1-\eta}{\eta}} \Rightarrow \eta\beta = 1 - \eta \Rightarrow \eta\beta + \eta = 1 \Rightarrow \boxed{\eta = \frac{1}{\beta + 1}}$$

SOLVED PROBLEMS

A certain engine which operates in a Carnot cycle absorbs 4 kJ at 527°C how much work is done on the engine per cycle and how much heat is evolved at 127°C in each cycle?

Soln. The efficiency of the Carnot cycle is given by

$$\eta = \frac{T_2 - T_1}{T_2} = \frac{q_2 + q_1}{q_2}$$

Thus, $-\frac{T_1}{T_2} = \frac{q_1}{q_2}$ and hence $q_1 = -\left(\frac{T_1}{T_2}\right) q_2$

Thus, the heat evolved in the present case is

$$q_1 = -\left(\frac{400K}{800K}\right)(4kJ) = -2kJ$$

and the work done on the engine is

$$w = -(q_2 + q_1) = -4 + 2 = -2kJ$$

The negative sign indicates that the work is actually done by the engine.

2. What % of T_1 of T_2 for a 10% efficiency?

Soln. $\eta = 1 - \frac{T_1}{T_2} \Rightarrow \frac{10}{100} = 1 - \frac{T_1}{T_2}$

$$\Rightarrow \quad \frac{T_1}{T_2} = 1 - \frac{10}{100} = \frac{90}{100} = 0.9$$

$T_1 = .9T_2 \Rightarrow T_1\% = .9T_2 \times 100$

$\Rightarrow \quad \boxed{T_1\% = 90\%T_2}$

3. Calculate the maximum efficiency of an engine operating between 110°C and 25°C.

Soln. Maximum efficiency of an engine working between temperatures T_2 and T_1 is given by

$$\eta = (T_2 - T_1)/T_2 = (383K - 298K)/383K = 0.222 = 22.2\%$$

4. Heat supplied to a Carnot engine is 1897.8 kJ. How much useful work can be done by the engine which works between 0°C and 100°C?

Soln. $T_2 = 100 + 273 = 373K; T_1 = 0 + 273 = 273K; q_2 = 1897.8\ kJ$

$$w = q_2(T_2 - T_1)/T_2 = 1897.8\ kJ \times (373K - 273K)/373K = 508.7\ kJ$$

Therefore, work done by the engine = 508.7 kJ

An important generalisation

$$1 - \left(\frac{q_1}{q_2}\right) = 1 - \left(\frac{T_1}{T_2}\right) \text{ or } \frac{q_1}{T_1} = \frac{q_2}{T_2} \qquad \text{... (i)}$$

Equation (i) may also be written, in the general form, as

$$\frac{q_{rev}}{T} = \text{constant}$$

where q_{rev} is the quantity of heat exchanged in a process carried out reversibly at a temperature T. This is an important generalisation since the quantity $\frac{q_{rev}}{T}$, as well shall see presently, represents a definite quantity or state function, the entropy change of the system.

5. A Carnot cycle operates on a temperature difference of 200K. One-third of the heat absorbed from the source at T_2 is discharged as waste heat to the sink at T_1. The cycle does 400J of work. Calculate q_1, q_2, T_1 and T_2.

[GATE 1996]

Soln. Given, $Q_h = Q$ (for source)

$$Q_c = \frac{Q}{3} \quad \text{(for sink)}$$

$w = -400J$ and $\Delta T = 200K$

$\because \quad \eta = 1 - \frac{Q_c}{Q_h} = 1 - \frac{Q}{3Q} \Rightarrow \eta = \frac{2}{3}$

$\because \quad \eta = \frac{T_h - T_c}{T_h}$ or $\frac{2}{3} = \frac{200}{T_h}$ or $T_h = 300$

$\Delta T = T_h - T_c$

$200 = 300 - T_c$

$\therefore \quad T_c = 100$

Since, $\eta = -\frac{w}{+Q_h} \Rightarrow \frac{2}{3} = -\frac{(-400)}{Q_h} \Rightarrow Q_h = 600$

$\therefore \quad Q_c = \frac{600}{3} = 200$

6. A Carnot engine operates between 600K and 800K and absorbs 2, 000 calories from the source per cycle. The work done (in Cal) per cycle is **[GATE 1998]**

(a) 1, 000 (b) 500 (c) 666 (d) 2, 000

Soln. Since, $\eta = \frac{T_h - T_c}{T_h}$

$$\eta = \frac{800-600}{800} = \frac{200}{800} = \frac{1}{4} \quad \Rightarrow \eta = \frac{-w}{+Q_h}$$

$$\frac{\eta}{4} = \frac{-w}{2000} \text{ or } \boxed{w = 500\ cal}$$

Correct option is (b)

7. The coefficient of performance of a perfect refrigerator working reversibly between the temperatures T_c and T_h is given by **[GATE 2004]**

(a) $\frac{T_c - T_h}{T_c}$ (b) $\frac{T_h - T_c}{T_c}$ (c) $\frac{T_c}{T_h - T_c}$ (d) $\frac{T_h}{T_h - T_c}$

Soln. The ratio of heat transferred from a lower temperature to a higher temperature to the work done on the machine to cause this removal, i.e. $\beta = \frac{|q_C|}{w}$

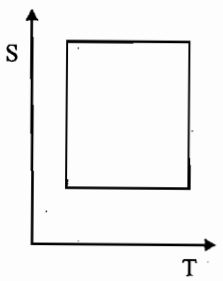
The less the work done the more efficient the operation and greater the coefficient of performance.

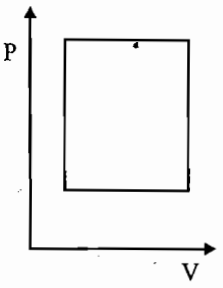
$\because \quad w_{irr} > w_{rev}, \quad \therefore \quad \beta_{rev} > \beta_{irr}$

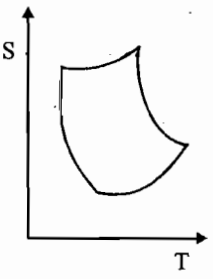
$$\beta = \frac{|q_C|}{|q_h| - |q_C|} = \frac{T_c}{T_h - T_c}$$

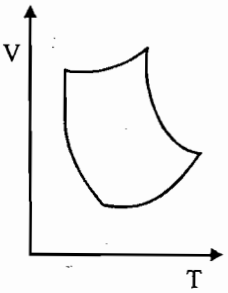
Correct option is (c)

8. The plot that describes a Carnot cycle is: **[GATE 2006]**

(a) 

(b) 

(c) 

(d) 

Soln. **Correct option is (a)**

9. In a carnot engine 200 cal heat is given to the sink by a reservoir at 27°C. If temperature of the source is 57°C, then find:

(i) How much heat flows from the source.

(ii) Efficiency of the engine

(iii) Work done by the reservoir.

Soln : Here, given, $Q_2 = 200$ cal, $Q_1 = ?$

$T_2 = 27°C = (27 + 273) = 300K$

$T_1 = 57°C = (57 + 273) = 330K$; $\eta = ?$ and $W = ?$

(i) We have, $\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$

$\Rightarrow \quad \frac{Q_1}{330K} = \frac{200cal}{300K} \Rightarrow \frac{Q_1}{11} = \frac{200}{10}cal \quad \Rightarrow Q_1 = 220$ cal

(ii) $\eta = 1 - \frac{Q_2}{Q_1} \Rightarrow \eta = 1 - \frac{200}{220} \Rightarrow \eta = 1 - \frac{10}{11} \Rightarrow \eta = \frac{1}{11}$

(iii) $W = Q_1 - Q_2 = (220 - 200)cal = 20cal$

OR

(ii) $\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{300}{330} = 1 - \frac{10}{11} = \frac{1}{11}$

(i) $\eta = 1 - \frac{Q_2}{Q_1} \Rightarrow \frac{1}{11} = 1 - \frac{200}{Q_1} \Rightarrow 1 - \frac{1}{11} = \frac{200}{Q_1} \Rightarrow \frac{10}{11} = \frac{200}{Q_1} \Rightarrow Q_1 = 220cal$

(iii) $W = Q_1 - Q_2 = (220 - 200)cal = 20cal$

10. Temperature of the sink of a carnot engine is 7°C and efficiency is 50%, then calculate change in temperature of the source to increase the efficiency of the same engine 70%.

Soln. We know that $\eta = 1 - \frac{T_{sink}}{T_{source}}$ ... (i)

Case-I: $\eta = 50\% = \frac{50}{100} = \frac{1}{2} \Rightarrow T_{sink} = 7°C = (7 + 273)\ K = 280K$

from equation (i), $\frac{1}{2} = 1 - \frac{280K}{T_{source}}$

$$\frac{280K}{T_{source}} = 1 - \frac{1}{2} = \frac{1}{2} \Rightarrow T_{source} = 560K$$

Case-II: $\eta = 70\% = \frac{70}{100} = \frac{7}{10} \Rightarrow T_{sink} = 7°C = (7 + 273)\ K = 280K$

from equation (i)

$$\Rightarrow \quad \frac{7}{10} = 1 - \frac{280K}{T_{source}} \Rightarrow \frac{280K}{T_{source}} = 1 - \frac{7}{10} = \frac{3}{10}$$

$$\Rightarrow \quad T_{source} = \frac{280K \times 10}{3 \times 1} \Rightarrow T_{source} = 933.33K$$

$\Rightarrow$ Change in temperature of the source = $(933.33 - 560)K = 373.33K$

11. The efficiency of a carnot's cycle is 1/6. If on reducing the temperature of the sink by 75K, efficiency becomes $\frac{1}{3}$, then find initial and final temperature between which the cycle is working.

Soln: We have, $\eta = 1 - \frac{T_2}{T_1} \Rightarrow \frac{1}{6} = 1 - \frac{T_2}{T_1} \Rightarrow \frac{T_2}{T_1} = 1 - \frac{1}{6} \Rightarrow \frac{T_2}{T_1} = \frac{5}{6}$

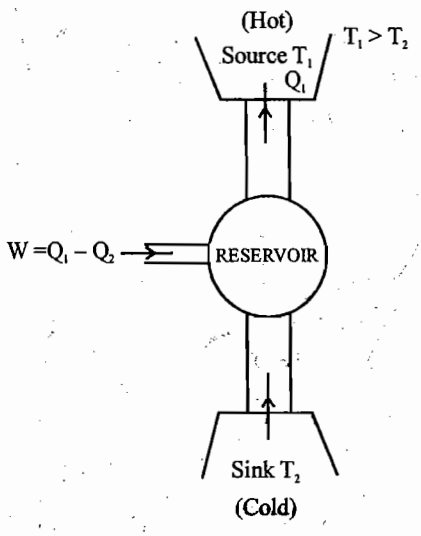
Now, $\eta = 1 - \frac{T_2 - 75}{T_1} \Rightarrow \frac{1}{3} = 1 - \frac{T_2}{T_1} + \frac{75}{T_1} \Rightarrow \frac{1}{3} = 1 - \frac{5}{6} + \frac{75}{T_1}$ [Using equation (i)]

$$\Rightarrow \quad \frac{1}{3} = \frac{1}{6} + \frac{75}{T_1} \Rightarrow \frac{75}{T_1} = \frac{1}{3} - \frac{1}{6} \Rightarrow \frac{75}{T_1} = \frac{1}{6} \Rightarrow T_1 = 450\ k$$

(ii) $\Rightarrow T_2 = \frac{5}{6} \times 450\ K = 5 \times 75\ K = 375\ K$

12. A Carnot refrigerator takes heat from water 0°C and discard it to a room at 27°C. 1 kg of water at 0°C is to be changed into ice at 0°C. How many calories of heat is discarded to the room? What is the work done by the refrigerator? In this process what is the value of cop?

Soln:



Here $T_1 = 27°C = 300K$, $T_2 = 0°C = 273K$

1kg 0°C Water → 0°C ice

$\therefore \quad Q_2 = 1 \times 10^3\ g \times 80\ \frac{Cal}{g} \Rightarrow Q_2 = 8 \times 10^4\ Cal$

We have, $\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \Rightarrow Q_1 = Q_2 \times \frac{T_1}{T_2} \Rightarrow Q_1 = 8 \times 10^4\ cal \times \frac{300}{273}$

$\therefore \quad$ Work done $= Q_1 - Q_2 = 8 \times 10^4 \times \frac{300}{273}\ Cal - 8 \times 10^4\ Cal = 8 \times 10^4 \times \left[\frac{300}{273} - 1\right] Cal$

$$= 8 \times 10^4 \times \left[\frac{27}{273}\right] Cal = \frac{72}{91} \times 10^4\ Cal = 0.79 \times 10^4\ Cal$$

and $\quad Cop\ (\beta) = \frac{Q_2}{Q_1 - Q_2} = \frac{8 \times 10^4 Cal}{8 \times 10^4 \left[\frac{300}{273} - 1\right] Cal} = \frac{273}{27} = \frac{91}{9} \approx 10$

13. A Carnot engine operates at 55% efficiency. If the temperature of reject steam is 105°C, then the absolute temperature of input steam is _____ **[GATE 2014]**

Soln. We know that,

Efficiency of carnot engine,

$$\eta = 1 - \frac{T_2}{T_1} \qquad \ldots (1)$$

Given, $\eta = 55\% = 0.55$

And $T_2 = 105 + 273 = 378K$

From equation (1),

$$0.55 = 1 - \frac{378}{T_1} K \quad \Rightarrow 0.55 - 1 = -\frac{378}{T_1} K$$

$$\Rightarrow \qquad -0.45 = -\frac{378}{T_1} \Rightarrow T_1 = \frac{378}{0.45} = 840K$$

Concept of Entropy :

Since we know that if $\oint dZ = 0$, then dZ is an exact differential and Z is a state function. Similarly, we can conclude that $q(rev)/T$ represents a state function because the value of its differnetial $d\left(q(rev)/T\right)$ over a cyclic process is zero. This state function is given the name entropy of the system and is represented by the symbol *S*. Thus

$$dS = d\left(\frac{q(rev)}{T}\right) \text{ and } S = \frac{q(rev)}{T}$$

The entropy function is a function of the independent variables which are used to define the state of a system. It is an extensive function. The change in the value of the entropy function in going from one state to another, is independent of the path, and the cyclic integral of dS for a cyclic change of state is always zero.

Unit of Entropy:

The unit of entropy function is energy unit divided by temperature unit.

For example : JK^{-1}, cal K^{-1}. A unit of 1 cal K^{-1} (non-SI) is known as an entropy unit and is represented by the symbol eu.

The value of $\frac{dq(irr)}{T}$ for an irreversible cyclic process :

If there is any irreversibility at any stage of a cycle, the net work obtained $|w_{net}|$ in the cycle is less than the maximum work obtainable from the reversible cycle operating between the same two temperatures. Consequently, the efficiency of an irreversible cycle is always less than the efficiency of the corresponding reversible cycle. It follows that

$$\frac{|w_{net}|}{q_2} < \frac{T_2 - T_1}{T_2} \text{ or } \frac{q_2 + q_1}{q_2} < \frac{T_2 - T_1}{T_2}$$

Or, $\qquad \frac{q_1}{q_2} < -\frac{T_1}{T_2}$ or $\frac{q_2}{T_2} + \frac{q_1}{T_1} < 0$

In the limiting case of infinitesimal heat transfer, this inequality becomes

$$\oint \frac{dq(irr)}{T} < 0$$

The fact that the sum of $\frac{q_2}{T_2}$ and $\frac{q_1}{T_1}$ is zero for a reversible Carnot cycle and is negative for a cycle involving irreversible isothermal expansion or/and irreversible isothermal compression may be rationalized as follows.

Since, in the isothermal reversible process of a Carnot cycle, the heat transferred is directly proportional to the temperature, we have $\frac{q_2}{T_2}$ = constant and $\frac{q_1}{T_1}$ = – constant (since q_1 is negative).

It follows that the sum of $\frac{q_2}{T_2}$ and $\frac{q_1}{T_1}$ is zero.

In an irreversible cycle operating between the same two temperatures T_1 and T_2, we have

(i) $q_2(irr) < q_2(rev)$ and hence $q_2(irr)/T_2$ will be less positive as compared to the value of $q_2(rev)/T_2$

(ii) $q_1(irr) < q_1(rev)$ or $|q_{irr}| > |q_{rev}|$ and hence $q_1(irr)/T_1$ will be more negative as compared to the value of $q_1(rev)/T_1$.

Thus, in a cycle involving either of these two irreversible steps or involving both of these steps, the sum

$$\frac{q_2(irr)}{T_2} + \frac{q_1(irr)}{T_1}$$

will always be negative, because $q_1(irr)/T_1$ is negative and its magnitude is greater than $q_2(irr)/T_1$.

A General Proof for reversible process $\oint dq(rev)/T = 0$ and irreversible process $\oint dq(irr)/T < 0$:

We have seen that for a Carnot cycle

$$-w = \oint dq \text{ and } \oint \frac{dq(rev)}{T} = 0 \quad \ldots (i)$$

Now consider any other cycle, howsoever complicated (containing any number of temperature reservoirs and any working substance). For this engine, according to the first law, we have

$$-w' = \oint dq' \quad \ldots (ii)$$

and let for this engine.

$$\oint \frac{dq'}{T} > 0 \quad \ldots (iii)$$

The two engines are coupled together to make a composite cyclic engine, represented by the symbol, 'cyc'. The work involved in the composite cyclic engine is

$$w_{cyc} = w + w'$$

which, by equation (i) and (ii), are equal to

$$-w_{cyc} = \oint dq + \oint dq' = \oint dq(cyc) \quad \ldots (iv)$$

If equation, (i) and (iii) are added, we get

$$\oint \left(\frac{dq(rev)}{T} + \frac{dq'}{T} \right) > 0 \text{ or } \oint \frac{dq(cyc)}{T} > 0$$

If it is adjusted that the composite cyclic engine does not produce any work, then $w_{cyc} = 0$. With this condition, equation (iv) becomes

$$\oint dq(cyc) = 0 \quad \ldots (v)$$

Since each of the cyclic integral can be considered as a sum of terms, we may write equation (v) and (iv) as

$$q_1 + q_2 + q_3 + \ldots\ldots = 0 \quad \ldots (vi)$$

$$\frac{q_1}{T_1} + \frac{q_2}{T_2} + \frac{q_3}{T_3} + \ldots\ldots > 0 \quad \ldots (vii)$$

The expression on the left hand side of equation (vi) includes a number of terms, some positive and some negative. The positive ones just balance the negative ones and the sum is zero.

In equation (vii) the net sum can be positive only if the positive terms are divided by small numbers and negative terms are divided by large numbers. This amounts to the fact that we are associating positive values of q with low temperature and negative values with high temperatures. This is against the second law of thermodynamics. Thus, our approximation that

$$\oint \frac{dq'}{T} > 0$$

must be wrong. It follows that for any engine, we must have

$$\oint \frac{dq'}{T} \leq 0$$

Now we will show that for a reversible cycle $\oint dq'/T = 0$ whereas $\oint dq'/T < 0$ for an irreversible cycle.

Case-I : Reversible cycle. Let us assume for this cycle

$$\oint \frac{dq}{T} < 0$$

We can reverse this engine, which changes all the signs but not the magnitudes of the qs. Thus, we have,

$$\oint \frac{dq}{T} > 0$$

which obviously is wrong as deduced earlier. This leads to the conclusion that for any system.

$$\oint \frac{dq(rev)}{T} = 0$$

for all reversible cycles.

Case-II : Irreversible cycle. Since the heat and work associated with an irreversible cycle are different from those associated with the reversible cycles, therefore, the only possibility left is

$$\oint \frac{dq'}{T} < 0$$

for all irreversible cycles.

Entropy and unavailable energy:

In the carnot cycle working between two temperatures T_2(source) and T_1(sink). If q_2 is heat absorbed from source at T_2 and q_1 be the heat rejected to the sink at T_1, then work done is given by

$$-w = q_2 - q_1 = \text{energy available for doing useful work}$$

$\therefore$ q_1 = unavailable portion of heat i.e. unavailable energy

$$\eta = 1 - \frac{q_1}{q_2} = 1 - \frac{T_1}{T_2}$$

$$\therefore \quad \frac{q_1}{q_2} = \frac{T_1}{T_2} \Rightarrow \frac{q_1}{T_1} = \frac{q_2}{T_2}$$

$$\Rightarrow \quad q_1 = \left(\frac{q_2}{T_2}\right).T_1 \qquad \ldots (1)$$

Thus for a given sink (T_1), unavailable energy (q_1) is determined by (q_2/T_2). Hence entropy is unavailable energy of system, i.e. law of increase of entropy for irreversible processes is connected with the law of dissipation of energy. Therefore, the second law of thermodynamics says that entropy is a measure of unavailable energy.

Spontaneous (irreversible) process and non-spontaneous (irreversible) process:

The process which proceed by themselves and bring the system closer to the equilibrium are called spontaneous process. All natural process are spontaneous.

The process which can't proceed by themselves are called non-spontaneous process. These require external force and brings the system away from equilibrium.

$\Rightarrow$ In spontaneous processes entropy of universe is completely increasing i.e. unavailable energy goes on increasing and the workable energy is continuously decreasing. A spontaneous process comes to an end at equilibrium, and since at equilibrium the entropy is maximum, it can be remarked that nature is trying to attain the state of maximum entropy.

$\Rightarrow$ Entropy is a state function

$\therefore \quad dS = \frac{dq}{T}$ = an exact differential

$\Rightarrow$ Entropy is an extensive property.

$\Rightarrow$ Entropy of reaction:

$$\Delta S_{(\text{reaction})} = \sum^{\text{Product}} n\,S - \sum^{\text{Reactant}} m\,S$$

S = absolute entropies of respective substances.

n and m = moles of products and reactants respectively

For a reaction, $m_1A + m_2B \longrightarrow n_1C + n_2D$

$$\Delta S_{(\text{reaction})} = \left[n_1S_{(C)} + n_2S_{(D)}\right] - \left[m_1S_{(A)} + m_2S_{(B)}\right]$$

Entropy changes in reversible process:

Let us consider an isothermal reversible process. In this the system absorbs heat q from surroundings at temperature T. This results in an increase in the entropy of system given by.

$$\Delta S_{\text{system}} = \frac{+q}{T}$$

$$\Delta S_{\text{surroundings}} = \frac{-q}{T}$$

Total entropy of the process = $\Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$

$$\Delta S_{\text{process}} = \frac{q}{T} + \left(\frac{-q}{T}\right)$$

$\therefore \quad \boxed{\Delta S_{\text{process}} = 0}$ ... (1)

Entropy changes in an irreversible processes:

Let q amount of heat is transferred from system which is at higher temperature (T_2) to the surroundings which is at lower temperature (T_1)

$\therefore$ Decrease in entropy of system $= \frac{-q}{T_2}$

Incease in entropy of surroundings $= \frac{+q}{T_1}$

$\therefore$ Net entropy change of process = $\Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$

$$\Delta S_{process} = \frac{-q}{T_2} + \frac{q}{T_1} = q\left[\frac{1}{T_1} - \frac{1}{T_2}\right] = q\left[\frac{T_2 - T_1}{T_1 . T_2}\right]$$

$\because$ $T_2 - T_1 = +ve$

$\therefore$ $\boxed{\Delta S_{process} = +ve}$ or $\boxed{\Delta S > 0}$ ... (2)

Combining equation (1) and (2)

$\boxed{\Delta S_{process} \geq 0}$

Adiabatic processes are isoentropic:

$\because$ $dS = \frac{dq}{T}$

For adiabatic process $dq = 0$

$\therefore$ $\boxed{dS = 0}$ or $S = \text{constant}$

Relation between $\left(\frac{\partial S}{\partial V}\right)_T$ expansion coefficient (α) and isothermal compressibility (β):

$$\boxed{\left(\frac{\partial S}{\partial V}\right)_T = \frac{\alpha}{\beta}}$$

Problem : For $C_6H_6(\ell)$, $\alpha = 1\times10^{-3} K^{-1}$ and $\beta = 9\times10^{-4} MPa^{-1}$ at 300 K and 101.325 kPa pressure. Find the change in molar volume which will be required to produce an entropy change of $2JK^{-1}mol^{-1}$ at 270 K. Assume α and β to be constants.

Soln. We know that, $\left(\frac{\partial S}{\partial V}\right)_T = \frac{\alpha}{\beta}$

Or, $\frac{\Delta S}{\Delta V} = \frac{\alpha}{\beta}$

$$\Delta V = \frac{\Delta S \cdot \beta}{\alpha} = \frac{2JK^{-1}mol^{-1} \times 9\times10^{-4} MPa^{-1}}{1\times10^{-3}\ K^{-1}} = 1.8\ cm^3 mol^{-1}$$

Entropy as a function of temperature and pressure :

Since, we know that dependence of entropy on temperature and pressure as

$$S = f(T, p)$$

On differentiating, we get

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \quad \text{... (i)}$$

In order to write the equation,

$$dS = \frac{1}{T} dU + \frac{P}{T} dV \quad \text{... (ii)}$$

From equation (i), we consider the following relation.

$$U = H - PV$$

$$\Rightarrow \quad dU = dH - PdV - VdP$$

Taking $H = f(T, P)$, we get

$$dU = \left\{\left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP\right\} - PdV - VdP \quad \text{... (iii)}$$

Substituting equation (3) in equation (2), we get

$$dS = \frac{1}{T}\left\{\left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP\right\} - \frac{P}{T}dV - \frac{V}{T}dP + \frac{P}{T}dV$$

Or,

$$dS = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P dT + \frac{1}{T}\left\{\left(\frac{\partial H}{\partial P}\right)_T - V\right\}dP$$

Comparing this with equation (1), we get

$$\boxed{\left(\frac{\partial S}{\partial T}\right)_P = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P = \frac{nC_P}{T}} \quad \text{... (iv)}$$

And

$$\boxed{\left(\frac{\partial S}{\partial P}\right)_T = \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]}$$

Entropy change in an isobaric variation in temperature :

Equation (iv) gives the dependence of entropy on temperature at constant pressure. Since both C_P and T are positive, therefore, S increases with increase in temperature of the system when the pressure is held constant. For a finite change of temperature at constant pressure, we have

$$\boxed{\Delta S = \int_{T_1}^{T_2} \frac{nC_P}{T} dT}$$

For C_P :

Case-I : If C_P is considered independent of temperature in the range T_1 to T_2, then

$$\Delta S = nC_P \ln \frac{T_2}{T_1}$$

Case-II : If temperature dependence of C_P is available in the form of the analytic expression.

$$C_P = a + bT + cT^2 + ...$$

Then we have,

$$\Delta S = \int_{T_1}^{T_2} n \frac{\left(a + bT + cT^2 + ...\right)}{T} dT$$

$$\boxed{\Delta S = n\left[a \ln \frac{T_2}{T_1} + b\left(T_2 - T_1\right) + \frac{c}{2}\left(T_2^2 - T_1^2\right) + ...\right]}$$

Problem : Calculate ΔS for 2 mol of nitrogen heated at constant pressure from 300 K to 400 K. Given the temperature variation of C_P of nitrogen as

$$C_P / JK^{-1}mol^{-1} = 20 + 4\left(\frac{T}{K}\right) - 2 \times 10^{-3}\left(\frac{T}{K}\right)^2$$

Soln. Since, we know that,

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$

Substituting the given expression of C_p, we get

$$\left(\frac{\partial S}{\partial T}\right)_P / JK^{-1}\, mol^{-1} = \left(\frac{20}{T}\right) + 4/K - 2\times10^{-3}\left(\frac{T}{K^2}\right)$$

$$\frac{dS}{JK^{-1}mol^{-1}} = \left(\frac{20}{T} + \frac{4}{K} - 2\times10^{-3}\left(\frac{T}{K^2}\right)dT\right)$$

On integrating this we have,

$$= \int_{300K}^{400K}\left(\frac{20}{T} + \frac{4}{K} - 2\times10^{-3}\left(\frac{T}{K^2}\right)dT\right)$$

$$= \left[20\ln\left(\frac{T}{K}\right)\right]_{300K}^{400K} + \left[4\left(\frac{T}{K}\right)\right]_{300K}^{400K} - \left[2\times10^{-3}\left(\frac{T^2}{K^2}\right)\right]_{300}^{400}$$

$$= 20\times2.303\times\log\left(\frac{400}{300}\right) + 4(400-300) - 2\times10^{-3}\left[(400)^2 - (300)^2\right]$$

$$= 46.06\times0.124 + 4\times100 - 2\times10^{-3}(400-300)(400+300)$$

$$= 5.70 + 400 - 2\times100\times700\times10^{-3}$$

$$= 405.70 - 140 = 265.70\, JK^{-1}$$

Combination of first and second law:

For a reversible process

(i) According to first law, dq = dE + PdV

(ii) According to second law, $dS = \frac{dq}{T}$

From these two, $dS = \frac{dE + PdV}{T}$

$$\boxed{TdS = dE + PdV} \qquad \ldots (1)$$

Entropy change for ideal gas in different cases:

$\because$ $$dS = \frac{dq}{T} = \frac{du + PdV}{T}$$

$$dS = \frac{nC_V dT + PdV}{T} \qquad \ldots (A)$$

Or, $$dS = nC_V\frac{dT}{T} + \frac{PdV}{T} \qquad \left[\because P = \frac{nRT}{V}\right]$$

Or, $$dS = nC_V\frac{dT}{T} + nR\frac{dV}{V}$$

Integrating it without limit and taking limit.

$$\int dS = \int nC_V\frac{dT}{T} + \int nR\frac{dV}{V}$$

Or, $\boxed{S = nC_V \ln T + nR \ln V + S_0}$

For with limit,

$$\int_{S_1}^{S_2} dS = \int_{T_1}^{T_2} nC_V \frac{dT}{T} + nR \int_{V_1}^{V_2} \frac{dV}{V}$$

Or, $$S_2 - S_1 = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

Or, $$\boxed{\Delta S = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}} \quad \text{.... (1)}$$

Equation (1) is reversible, ideal but isothermal.

$\because$ $$P_1V_1 = nRT_1 \quad \text{... (2)}$$

$$P_2V_2 = nRT_2 \quad \text{... (3)}$$

From equation (2) and (3), we get

$$\frac{P_2V_2}{P_1V_1} = \frac{T_2}{T_1} \Rightarrow \frac{V_2}{V_1} = \frac{T_2}{T_1} \cdot \frac{P_1}{P_2}$$

From (2),

$$\Delta S = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$$

$$\Delta S = n\left(C_V + R\right) \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$$

$$\boxed{\Delta S = nC_P \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}}$$

$\because$ $$PV = nRT$$

$$PdV + VdP = nRdT$$

$$PdV = nRdT - VdP$$

From (A),

$$dS = \frac{nC_V dT + nRdT - VdP}{T}$$

Or, $$dS = \frac{n\left(C_V + R\right)dT - VdP}{T}$$

Or, $$dS = \frac{nC_P dT - VdP}{T}$$

Or, $$dS = nC_P \frac{dT}{T} - V\frac{dP}{T} \qquad \left(\because V = \frac{nRT}{P}\right)$$

Or, $$dS = nC_P \frac{dT}{T} - \frac{nRT}{P}\frac{dP}{P}$$

Or, $$dS = nC_P \frac{dT}{T} - nR\frac{dP}{P}$$

For without limit,

$$\int dS = \int nC_P \frac{dT}{T} - \int nR \frac{dP}{P}$$

Or, $$S = nC_P \ln T - nR \ln P + S_0$$

For limit,

$$\int_{S_1}^{S_2} dS = \int_{T_1}^{T_2} nC_P \frac{dT}{T} - \int_{P_1}^{P_2} nR \frac{dP}{P}$$

(i) Isothermal Process:

In isothermal Process T = constant

$$\Rightarrow \quad T_1 = T_2 = T \quad \Rightarrow \quad \ln\left(\frac{T_2}{T_1}\right) = \ln(1) = 0$$

from equation (1)

$$\boxed{\Delta S_{isothermal} = nR \ln\left(\frac{V_2}{V_1}\right)}$$

(ii) Isochoric Process:

In isochoric process

$$V = \text{Constant} \quad \Rightarrow \quad V_1 = V_2 = V$$

$$\Rightarrow \quad \Delta S_{isochoric} = n\, C_V \ln\left(\frac{T_2}{T_1}\right) + n\, R \ln\left(\frac{V}{V}\right)$$

$$\Rightarrow \quad \Delta S_{isochoric} = n\, C_V \ln\left(\frac{T_2}{T_1}\right) + n\, R \ln \ln 1$$

$$\Rightarrow \quad \Delta S_{isochoric} = nC_V \ln\left(\frac{T_2}{T_1}\right) + n\, R \ln\left(\frac{V}{V}\right)$$

$$\Rightarrow \quad \Delta S_{isochoric} = n\, C_V \ln\left(\frac{T_2}{T_1}\right) + 0$$

$$\Rightarrow \quad \boxed{\Delta S_{isochoric} = nC_V \ln\left(\frac{T_2}{T_1}\right)}$$

Now, ideal gas equation is

$$PV = n\,RT$$

$$\Rightarrow \quad P_1 V_1 = n\,RT_1 \qquad \text{... (ii)}$$

$$\Rightarrow \quad P_2 V_2 = n\,RT_2 \qquad \text{... (iii)}$$

From equation (iii) and (ii), we get

$$\frac{T_2}{T_1} = \frac{P_2 V_2}{P_1 V_1}$$

Now making substitution in equation (i), we get

$$\Delta S = n\,CV \ln\left(\frac{P_2}{P_1} \cdot \frac{V_2}{V_1}\right) + nR \ln\left(\frac{V_2}{V_1}\right)$$

$$\Rightarrow \quad \Delta S = n\, C_V \ln\left(\frac{P_2}{P_1}\right) + nC_V \ln\left(\frac{V_2}{V_1}\right) + n\, R \ln\left(\frac{V_2}{V_1}\right)$$

$\Rightarrow \quad \Delta S = n C_V \ln\left(\frac{P_2}{P_1}\right) + n(C_V + R)\ln\left(\frac{V_2}{V_1}\right)$

$\Rightarrow \quad \boxed{\Delta S = n C_V \ln\left(\frac{P_2}{P_1}\right) + n C_P \ln\left(\frac{V_2}{V_1}\right)} \quad (\because C_P - C_V = R)$

This is the general express for the change in entropy for an ideal gas when pressure and volume (P&V) vary.

(iii) Isobaric process :

In isobaric process

$P = \text{constant} \Rightarrow P_1 = P_2 = P$

from equation (iv)

$\Rightarrow \quad \Delta S_{isobaric} = n C_V \ln\left(\frac{P}{P}\right) + n C_P \ln\left(\frac{V_2}{V_1}\right) \Rightarrow \Delta S_{isobaric} = n C_V \ln 1 + n C_P \ln\left(\frac{V_2}{V_1}\right)$

$\Rightarrow \quad \Delta S_{isobaric} = 0 + n C_P \ln\left(\frac{V_2}{V_1}\right) \quad \boxed{\Delta S_{isobaric} = n C_P \ln\left(\frac{V_2}{V_1}\right)}$

SOLVED PROBLEMS

1. Ten moles of a gas is allowed to expand from a state, A, at 10 atm and 300K, to a state B, at 100 atm and 600K. If the value of C_p is 6.995 Cal deg^{-1}. Calculate the entropy change of this process. **[GATE 1998]**

Soln. Since, $\Delta S = 2.303\, nC_P \ln\frac{T_2}{T_1} + 2.303\, nR \log\frac{P_1}{P_2}$

$$\Delta S = 2.303\times10\times6.955\log\frac{600}{300} + 2.303\times10\times8.314\log\frac{100}{10}$$

$\Rightarrow \quad \Delta S = 2.303\times10\times6.955\log\frac{2}{3} + 2.303\times10\times8.314\log10$

$\Rightarrow \quad \Delta S = 2.303\times10\times6.55[\log2 - \log3] + 2.303\times10\times8.314\times1$

$\Rightarrow \quad \Delta S = 160.1(0.301) + 191.47$

$\Rightarrow \quad \Delta S = 239.66\ J/K\text{-}mole$

2. For an irreversible adiabatic expansion of a perfect gas from volume V_1 to V_f the change in entropy of the gas is **[GATE 2001]**

(a) $nR\ln(V_f / V_i)$ (b) zero (b) less than zero (d) greater than zero

Soln. For irreversible adiabatic expansion entropy is greater than zero $(dS)_{irr} \geq 0$

Correct option is (d)

3. The change in entropy when one mole of an ideal gas is compressed to one-fourth of its intial volume and simultaneously heated to twice its initial temperature is **[GATE 2004]**

(a) $(C_V - R)\ln 4$ (b) $(C_V - 2R)\ln 2$ (c) $(C_V - 2R)\ln 4$ (d) $(C_V + 2R)\ln 2$

Soln. Since, we know that, $\Delta S = C_V \ln\frac{T_2}{T_1} + R\ln\frac{V_2}{V_1}$

Given, $V_1 = V,\ V_2 = \frac{V}{4},\ T_1 = T$ and $T = 2T$

$\therefore \quad \Delta S = C_V \ln\left(\frac{2T}{T}\right) + R\ln\frac{V}{4V} \Rightarrow \Delta S = C_V \ln 2 + R\ln\left(\frac{1}{4}\right) \Rightarrow \Delta S = C_V \ln 2 - R\ln 4$

$\Rightarrow \quad \Delta S = C_V \ln 2 - R\ln(2)^2 \Rightarrow \Delta S = \ln 2 - 2R\ln 2 \Rightarrow \Delta S = \ln 2(C_V - 2R)$

$\Rightarrow \quad \Delta S = (C_V - 2R)\ln 2$

Correct option is (b)

4. A box of volume V contains one mole of an ideal gas. The probability that all N particles will be found occupying one half of the volume leaving the other half empty is **[GATE 2008]**

(a) $\frac{1}{2}$ (b) $\frac{2}{N}$ (c) $\left(\frac{1}{2}\right)^N$ (d) $\left(\frac{1}{2}\right)^{6N}$

Soln. Occupation of n molecule out of N molecule in the volume V out of total V.

$$\frac{N!}{n!(N-n)!}\left(\frac{v}{V}\right)^n\left(\frac{V-v}{V}\right)^{N-n}$$ Total volume $= V$

$\therefore \quad v = \frac{V}{2}$ and $N = n$

$$\frac{N!}{N!(N-n)!}\left(\frac{v}{2V}\right)^N\left(\frac{V-V/2}{V}\right)^{N-n}$$

$\Rightarrow \quad 0!\left(\frac{1}{2}\right)^N\left(\frac{V}{2V}\right)^0$

$\Rightarrow \quad 0!\left(\frac{1}{2}\right)^N\left(\frac{1}{2}\right)^0 \qquad \left(\because 0! = 1 \text{ and } \left(\frac{1}{2}\right)^0 = 1\right)$

$\Rightarrow \quad 1\times\left(\frac{1}{2}\right)^N \times 1 \Rightarrow \left(\frac{1}{2}\right)^N$

Correct option is (c).

5. The change in entropy when two moles of Argon gas are heated at constant volume from 300 K to 500 K is: **[GATE 2010]**

(a) $-12.74\ JK^{-1}mol^{-1}$ (b) $-6.37\ JK^{-1}mol^{-1}$ (c) $6.37\ JK^{-1}mol^{-1}$ (d) $12.74\ JK^{-1}mol^{-1}$

Soln. Given, for Argon $C_V = 1.5R$, $n = 2$

$T_1 = 300K$ and $T_2 = 500K$

$$\Delta S = 2.303\, nC_V \log\frac{T_2}{T_1} = 2.303\times 2\times 1.5\times 8.314\times\log\frac{500}{300}$$

$= 57.44\times 0.22 = 12.74\ JK^{-1}mole$

$= 57.44[\log 500 - \log 300]$

$= (57.44)\times(-0.22) = -12.74\ JK^{-1}mole$

Correct option is (a)

6. For the process [GATE 2011]

$$1\,\mathrm{Ar}(300\mathrm{K}, 1\,\mathrm{bar}) \longrightarrow 1\,\mathrm{Ar}(200\mathrm{K}, 10\,\mathrm{bar})$$

assuming ideal gas behavior, the change in molar entropy is:

(a) $-27.57\ \mathrm{J\,K^{-1}\,mol^{-1}}$ (b) $+27.57\ \mathrm{J\,K^{-1}\,mol^{-1}}$

(c) $-24.20\ \mathrm{J\,K^{-1}\,mol^{-1}}$ (d) $+24.20\ \mathrm{J\,K^{-1}\,mol^{-1}}$

Soln. Argon is monoatomic gas, for monoatomic

$C_V = 1.5R$ and $C_P = 2.5R$

$$\because \quad \Delta S = 2.303\, C_P \log\frac{T_2}{T_1} + 2.303R\log\frac{P_1}{P_2}$$

$$\Delta S = 2.303\times 2.5\times 8.314\frac{J}{K\text{-}mole}\log\frac{200K}{300K} + 2.303\times 8.314\frac{J}{K\text{-}mole}\log\frac{1\,bar}{10\,bar}$$

$$\Delta S = 47.86\frac{J}{K\text{-}mole}[\log 200 - \log 300] + 19.15\frac{J}{K\text{-}mole}[\log 1 - \log 10]$$

$$= 47.86\frac{J}{K\text{-}mole}(-0.176) + 19.15\frac{J}{K\text{-}mole}(-1)$$

$$= -8.42\frac{J}{K\text{-}mole} - 19.15\frac{J}{K\text{-}mole} = -27.57\ JK^{-1}mole^{-1}$$

Correct option is (a)

7. The maximum non-PV work that a system can perform at constant P is [GATE 2014]

(a) ΔH (b) ΔG (c) ΔS (d) ΔA

Soln. From first law of thermodynamics

$$\Delta E = q + W$$

the work done, W may be expansion or non-explansion so

$$\Delta E = q + W_{expansion} + W_{non-expansion}$$

Or, $$q = \Delta E + p\Delta V + W_{\text{non-expansion}}$$

$$q = \Delta H - W_{non-\text{expansions}} \qquad (\because \Delta E + p\Delta V = \Delta H)$$

Since, we know that,

$$\Delta S = \frac{q_{rev}}{T}$$

Or, $$q_{rev} = \Delta ST$$

$$\therefore \quad T\Delta S = \Delta H - W_{\text{non-expansion}}$$

Or, $$W_{\text{non-expansion}} = \Delta H - T\Delta S \qquad (\because \Delta G = \Delta H - T\Delta S)$$

$$W_{\text{non-expansion}} = \Delta G$$

The non-expansion work is also termed as non-pv work or useful work.

The ΔG shows the maximum non-pv work that a system can perform at constant p.

8. The van der waals constant a and b of CO_2 are 3.64 L_2 bar mol^{-2} and 0.04 L mol^{-1}, respectively. The value of R is 0.083 bar $dm^3\ mol^{-1}K^{-1}$. If one mole of CO_2 is confined to a volume of 0.15L at 300K, then the pressure (in bar) exerted by the gas, is _____ [GATE 2014]

Soln. Given, $a = 3.64\ L^2 bar\ mol^{-2}$

$b = 0.04\ L\ mol^{-1}$

$R = 0.083\ bar\ dm^3\ mol^{-1}K^{-1}$

$T = 300K$ and $P = ?$

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

Van der Waals equation for 1 mole of a gas can be written as

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

On substituting values

$$\left[p + \frac{3.64}{(0.15)^2}\right](0.15 - 0.04) = 0.083 \times 300$$

$$\left(p + \frac{3.64}{0.0225}\right)(0.11) = 24.9$$

$p + 161.78 = 226.36$ or $p = 226.30 = 161.78 = 64.58\ bar$

Criteria for Reversible and Irreversible processes :

Since, we know that

$$dS = dq_{rev}/T = (dU + PdV)/T$$

For irreversible process,

$$TdS > dq_{rev}$$

We also write, $TdS = dU + PdV$ (for reversible process) ... (1)

$TdS > dU + PdV$ (for irreversible process) ... (2)

Combining (1) and (2), we have

$$TdS \geq dU + PdV \quad \text{... (3)}$$

(i) Criterion in terms of change of entropy : If U and V (internal energy and volume) remain constant, then, for an isothermal process (i.e., T is constant)

$$\boxed{(dS)_{u,v} \geq 0}$$

(ii) Criterion in terms of change of internal energy : If S and V (entropy and volume) are kept constant, then, for an isothermal process (i.e. T is constant)

$$\boxed{(dU)_{S,V} \leq 0}$$

(iii) Criterion in terms of change of enthalpy: If S and P are kept constant, the expression $TdS \geq dU + PdV$ may be written as

$$dU + PdV \leq 0$$

But $dU + PdV = dH$

$\therefore$ $$\boxed{(dH)_{S,P} \leq 0}$$

(iv) Criterion in terms of change of work function. Combining $TdS \geq dU + PdV$ with $dA = dU - TdS$ for an infinitesimally small change, we have

$$dA \le -PdV$$

At constant volume, therefore, $\boxed{(dA)_{V,T} \le 0}$

(v) Criterion in terms of change of free energy : Substituting for dG from $dG = dU + PdV + VdP - TdS - SdT$, $TdS \ge dU + PdV$, we have,

$$dG \le VdP - SdT$$

Therefore, at constant temperature and pressusre, $\boxed{(dG)_{P,T} \le 0}$

Remark:

$\Delta S_{H,P} \ge 0$	$\Delta P_{H,S} \ge 0$
$\Delta P_{G,T} \ge 0$	$\Delta V_{U,S} \le 0$
$\Delta V_{A,T} \le 0$	$\Delta T_{A,V} \le 0$
$\Delta T_{G,P} \le 0$	

PROBLEMS

1. The criterion for irreversibility for a process involving no work or pressure-volume work is **[GATE 1995]**

(a) $(dS)_{V,u} < 0$ (b) $(dS)_{V,u} > 0$ (c) $(dS)_{T,P} < 0$ (d) $(dS)_{T,V} > 0$

Soln. Correct option is (b)

2. Choose the correct criterion of spontaneity in terms of the properties of the system alone. **[GATE 2001]**

(a) $(dS)_{U,V} > 0$ (b) $(dS)_{T,P} > 0$ (c) $(dS)_{H,P} < 0$ (d) $(dG)_{T,V} < 0$

Soln. Correct option is (a)

3. The criterion for spontaneous change in terms of the state functions is: **[GATE 2004]**

(a) $dU_{S,V} \ge 0$ (b) $dA_{T,V} \ge 0$ (c) $dS_{U,V} \ge 0$ (d) $dG_{T,V} \le 0$

Soln. Correct option is (c)

Entropy - change in reversible phase transformation :

1. **Melting:**

(a) $\text{Solid} \underset{\Delta T_f}{\overset{\Delta H_f}{\rightleftharpoons}} \text{liquid}$

Since, $\Delta G = \Delta H - T\Delta S$ ... (1)

For equilibrium, $\Delta G = 0$, so from equation (1)

$$0 = \Delta H - T\Delta S \quad \Rightarrow \Delta H = T\Delta S \quad \Rightarrow \Delta S = \frac{\Delta H}{T}$$

$$\Rightarrow \boxed{\Delta S_{fusion} = \frac{\Delta H_{fusion}}{T_{fusion}}}$$

(b) $\text{liquid} \underset{T_f}{\overset{\Delta H_f}{\rightleftharpoons}} \text{solid}$

$$\boxed{\Delta S_{fusion} = -\frac{\Delta H_{fusion}}{T_{fusion}}}$$

2. Vaporisation:

(a) $\text{liquid} \underset{T_b}{\overset{\Delta H_v}{\rightleftharpoons}} \text{vapour}$

$$\boxed{\Delta S_v = \frac{\Delta H_v}{T_b}}$$ where, T_b is boiling point.

(b) $\text{vapour} \underset{T_b}{\overset{\Delta H_v}{\rightleftharpoons}} \text{liquid}$

$$\boxed{\Delta S_v = -\frac{\Delta H_v}{T_b}}$$

3. Sublimation:

(a) $\text{solid} \underset{T_{sub}}{\overset{\Delta H_{sub}}{\rightleftharpoons}} \text{vapour}$

$$\boxed{\Delta S_{sub} = \frac{\Delta H_{sub}}{T_{sub}}}$$

(b) $\text{liquid} \rightleftharpoons \text{vapour}$

$$\boxed{\Delta S_{sub} = -\frac{\Delta H_{sub}}{T_{sub}}}$$

Remark : $S_{vapour} - S_{liquid} = \frac{\Delta H_v}{T_b}$ Or, $\boxed{S_{vapour} = \frac{\Delta H_v}{T_b} + S_{liquid}}$

4. Allotropic transformation:

$$\text{Solid}(\alpha) \rightleftharpoons \text{Solid}(\beta)$$

α & β are two allotropic form of a solid.

$$\boxed{\Delta S_{Trans} = \frac{\Delta H_{trans}}{T_{trans}}}$$

ΔS_{tans} = entropy change for phase transformation process.

ΔH_{trans} = enthalpy change for phase transition at constant pressure & constant temperature.

T_{rans} = phase transition temperature

Entropy-change in irreversible phase transformation:

$$\underset{(T_1)}{\text{substance}(S)} \longrightarrow \underset{(T_2)}{\text{substance}(V)}$$

(i) $\underset{(T_1)}{\text{substance}(S)} \longrightarrow \underset{(T_f)}{\text{substance}(S)}$

In this condition, phase same, temperature different, $\boxed{\Delta S = C_{P,S} \ln \frac{T_f}{T_1}}$

(ii) $\underset{(T_f)}{\text{substance}(S)} \longrightarrow \underset{(T_f)}{\text{substance}(S)}$

In this condition phase differet and temperature same

$$\boxed{\Delta S = \frac{\Delta H_f}{\Delta T_f}}$$

(iii) $\underset{(T_f)}{\text{substance}(\ell)} \longrightarrow \underset{(T_b)}{\text{subtance}(\ell)}$

In this condition phase same, temperature different.

$$\boxed{\Delta S = C_{P,\ell} \ln \frac{T_b}{T_f}}$$

(iv) $\underset{(T_b)}{\text{substance}(\ell)} \rightleftharpoons \underset{(T_b)}{\text{substance}(v)}$

In this condition, phase same, temperature same.

$$\boxed{\Delta S = \frac{\Delta H_v}{T_b}}$$

(v) $\underset{(T_b)}{\text{substance}(v)} \rightleftharpoons \underset{(T_f)}{\text{substance}(v)}$

In this condition, phase same, temperature different.

$$\boxed{\Delta S = C_{P,V} \ln \frac{T_f}{T_b}}$$

Note :

(a) In adiabatic reversible process :

$$\Delta S_{system} = \Delta S_{surrounding} = \Delta S_{universe} = 0$$

(b) In adiabatic irreversible process:

$$\Delta S_{system} \geq 0;\ \Delta S_{universe} \geq 0 \text{ and } \Delta S_{surrounding} = 0$$

SOLVED PROBLEMS

1. Calculate the entropy change for the transformation $H_2O(\text{liq}, 1\text{ atm}) \rightarrow H_2O(g, 0.1\text{ atm})$ at 100°C. ΔH_{vap} for H_2O is 40670 J. **[GATE 1996]**

Soln. (i) $\underset{(100°C)}{H_2O(\ell, 1\text{ atm})} \longrightarrow \underset{(100°C)}{H_2O(g, 1\text{ atm})}$

$$\underset{(373K)}{H_2O(\ell, 1\text{ atm})} \longrightarrow \underset{(373K)}{H_2O(g, 1\text{ atm})}$$

$$\Delta S = \frac{\Delta H_{vap}}{T_b} = \frac{40670\text{J}}{373\text{K}} = 109.03\text{ J/K}$$

(ii) $\underset{(373K)}{H_2O(g, 1\text{ atm})} \longrightarrow \underset{(373K)}{H_2O(g, 0.1\text{ atm})}$

$$\Delta S = nR\ln\frac{P_1}{P_2} \Rightarrow \Delta S = 2.303\times 8.314\frac{J}{K\text{-mole}}\times\log\frac{1}{0.1} \qquad (\text{for 1 mole})$$

$$\Delta S = 2.303\times 8.314\frac{J}{K}\log 10$$

Therefore, total entropy, $\Delta S = (109 - 19.14)\,J/K = 128.14\,J/K$

2. Calculate the entropy change in the melting of 1 kg of ice at 0°C. Heat of fusion of ice $= 334.72\ Jg^{-1}$

Soln. $\Delta S_f = \dfrac{\Delta H_f}{T_f} = \dfrac{334.72\ J\ g^{-1}}{273K} = 1.226\ JK^{-1}g^{-1} = 1226\ JK^{-1}kg^{-1}$

3. Calculate the entroy increase in the evaporation of one mole of water at 100°C. Heat of vaporisation of water at 100°C = 2259.4 J g^{-1}.

Soln. $\Delta S_v = \dfrac{\Delta H_v}{T_b} = \dfrac{2259.4\ Jg^{-1}\times 18g\ mol^{-1}}{373K} = 109.03\ JK^{-1}mol^{-1}$

4. Calculate the entropy change accompanying the freezing of one mole of water at 25°C to ice at –10°C; given that the heat of fusion of ice at its fusion point (0°C) is 6.00 kJ mol^{-1}, the heat capacity of ice is 36.82 J K^{-1} mol^{-1} and heat capacity of liquid water is 75.31 J K^{-1} mol^{-1}.

Soln. (i) $\underset{(25°C)}{H_2O(\ell)} \longrightarrow \underset{(0°C)}{H_2O(\ell)}$

$$\underset{(298K)}{H_2O(\ell)} \longrightarrow \underset{(273K)}{H_2O(\ell)}$$

For this, $\Delta S = C_{P,\ell}\ln\dfrac{273K}{298K}$

$$\Rightarrow \quad \Delta S = 75.31\,JK^{-1}mol^{-1}\ln\frac{273}{298K}$$

$$\Rightarrow \quad \Delta S = 75.31 JK^{-1}mol^{-1}\ln(0.916)$$

$$\Delta S = -6.60 JK^{-1}mol^{-1}$$

(ii) $\underset{(273K)}{H_2O(\ell)} \longrightarrow \underset{(273K)}{H_2O(s)}$

$$\Delta S = -\frac{\Delta H_f}{T} = -\frac{6.00kJmol^{-1}}{273K} = \frac{6000Jmol^{-1}}{273K} = -21.97\ JK^{-1}mol^{-1}$$

(iii) $\underset{(273K)}{H_2O(s)} \longrightarrow \underset{(263K)}{H_2O(s)}$

$$\Delta S = C_{P,S}\ln\frac{263}{273} = (36.82\ JK^{-1}mol^{-1})\ln\frac{263}{273}$$

$$\Delta S = -1.50\ JK^{-1}mol^{-1}$$

Total change of entropy $\Delta S = -6.60JK^{-1}mol^{-1} + (-21.97)\,JK^{-1}(mol^{-1}) + (-1.50JK^{-1}mol^{-1})$

$$= -29.96JK^{-1}mol^{-1}$$

5. The criterion for the spontaneity of a process is **[GATE 2000]**

(a) $\Delta S_{sys} > 0$ (b) $\Delta S_{surr} > 0$ (c) $\Delta S_{sys} + \Delta S_{surr} > 0$ (d) $\Delta S_{sys} - \Delta S_{surr} > 0$

Soln. Correct option is (c)

6. ΔS^0_{univ} for the following reaction, at 298 K is: **[GATE 2006]**

$N_2 + 3H_2 \longrightarrow 2NH_3 \qquad \Delta S^0_{sys} = -197\ JK^{-1}, \quad \Delta H^0_{sys} = -91.8\ kJ$

(a) $-197\ J\ K^{-1}$ (b) $0\ J\ K^{-1}$ (c) $-308\ J\ K^{-1}$ (d) $111\ J\ K^{-1}$

Soln. Given, $\Delta S_{sys} = -197 JK^{-1}$ and $\Delta H_{sys} = -91.8\,kJ$

Since, we know that

$$\Delta S_{uni} = \Delta S_{sys} + \Delta S_{surr} = -197\ JK^{-1} + \frac{91.8\ kJ}{238\ K} \quad \left(\because \Delta S_{surr} = -\frac{\Delta H_{sys}}{T}\right)$$

$$= -197 JK^{-1} + \frac{91800J}{298K} = -197 JK^{-1} + 308 JK^{-1} = 111\ JK^{-1}$$

Correct option is (d)

7. The enthalpy of fusion of ice at 273K is 6.01 kJ mol^{-1} and the enthalpy of vaporization of water at 273K is 44.83 kJ mol^{-1}. The enthalpy of sublimation (in kJ mol^{-1}) of ice at 273K, is _____ **[GATE 2014]**

Soln. Given, $\underset{(273K)}{H_2O(s)} \longrightarrow \underset{(273K)}{H_2O(\ell)} \qquad \Delta H_1 = 6.01 kJmol^{-1}$

$\underset{(273K)}{H_2O(\ell)} \longrightarrow \underset{(273K)}{H_2O(g)} \qquad \Delta H_2 = 44.83\ kJmol^{-1}$

Therefore, enthalpy of sublimation of ice,

$\underset{(273K)}{H_2O(s)} \longrightarrow \underset{(273K)}{H_2O(s)} \Rightarrow \Delta H = \Delta H_1 + \Delta H_2 \quad \Rightarrow \Delta H = 6.01\ kJmol^{-1} \Rightarrow \Delta H = 50.84\ kJmol^{-1}$

Calculation of ΔS when vander waal gas heated and expanded simultaneously:

Consider n-moles of a vander waal gas, the temperature of gas is changed from T_1 to T_2 and at the same time the volume of gas changes from V_1 to V_2. This process is done at constant external pressure and in reversible manner. Then by first and second law:

$$TdS = dq_{rev} = dE + PdV \qquad \ldots (1)$$

Let $E = f(T, V)$

$$\Rightarrow \quad dE = \left(\frac{\partial E}{\partial T}\right)_V .dT + \left(\frac{\partial E}{\partial V}\right)_T .dV \qquad \left[\text{where, } C_V = \left(\frac{\partial E}{\partial T}\right)_V\right]$$

$$dE = C_V dT + \left(\frac{\partial E}{\partial V}\right)_T .dV \qquad \ldots (2)$$

from equations (1) and (2)

$$TdS = C_V .dT + \left(\frac{\partial E}{\partial V}\right)_T .dV + PdV$$

$$\therefore \quad dS = C_V\left(\frac{dT}{T}\right) + \frac{1}{T}\left[\left(\frac{\partial E}{\partial V}\right)_T + P\right]dV \qquad \ldots (3)$$

now for n-moles of vander waal gas.

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

$$P+\frac{n^2a}{V^2}=\frac{nRT}{(V-nb)} \quad \ldots (4)$$

Now, $\left(\frac{\partial E}{\partial V}\right)_T$ = internal pressure $\left(\pi=\frac{n^2a}{V^2}\right)$ for real gas.

therefore, from equation (3), we get

$$dS=C_V\left(\frac{dT}{T}\right)+\frac{1}{T}\left[\frac{n^2a}{V^2}+P\right]dV \quad \ldots (5)$$

from equations (4) and (5)

$$dS=C_V\left(\frac{dT}{T}\right)+\frac{1}{T}\left[\frac{nRT}{(V-nb)}\right]dV$$

$$\boxed{dS=C_V\left(\frac{dT}{T}\right)+\frac{nR}{(V-nb)}dV} \quad \ldots (6)$$

Taking C_V as independent of T, integrating equation (6) between suitable limits, we get

$$\Delta S=nC_V\left[\ell nT\right]_{T_1}^{T_2}+nR\left[\ell n(V-nb)\right]_{V_1}^{V_2}$$

$$\Delta S=nC_V\ell n\frac{T_2}{T_1}+nR\ell n\left[\frac{(V_2-nb)}{(V_1-nb)}\right] \quad \ldots (7)$$

Cases - I: When it expands isothermally, T is constant.

$\therefore$ $\Delta T=0$, then from equation (7), we get

$\Rightarrow$ $\boxed{\Delta S_T=nR\ell n\left(\frac{V_2-nb}{V_1-nb}\right)}$

Case - II: When V is constant; $(V_1-nb)=(V_2-nb)$

So, from equation (7), we get

$\therefore$ $\boxed{\Delta S_V=nC_V\ell n\frac{T_2}{T_1}}$.

Problem : One mole of a van der Waals gas undergoes a change from 298K and 1 dm^3 to 373K and 10 dm^3. What is the change in its entropy? Given, b = 0.06 $dm^3\ mol^{-1}$, C_V = 29.0 $J\ K^{-1}\ mol^{-1}$.

Soln. Since, we know that $\Delta S=C_V\ln\frac{T_2}{T_1}+R\ln\frac{V_2-b}{V_1-b}$

We get, $\Delta S=\left(29.0\ J\ K^{-1}\ mol^{-1}\right)\ln\frac{373}{298}+\left(8.314\ J\ K^{-1}mol^{-1}\right)\ln\left(\frac{10-0.06}{1-0.06}\right)$

$$=(6.51+19.61)JK^{-1}mol^{-1}=26.12\ J\ K^{-1}mol^{-1}$$

Entropy Change when two solids at different temperatures are brought together:

Consider two solid bodies of the same material each containing one mole of a substance. Let one be at higher temperature T_b and the other at lower temperature T_c. Let both of them be brought together. Heat will flow from the hotter body to the colder till the temperatures of both of them are the same. Let the equilibrium temeprature be T, the value of which can be calculated as follows:

Heat lost by hot body = Heat gained by cold body

$$m_h C_P (T_h - T) = m_c C_P (T - T_c)$$

Or, $$T = \frac{T_h + T_c}{2}$$

Consequently, entropy changes of two bodies are

$$\Delta S_h = C_P \ln \frac{T}{T_h} \Rightarrow \Delta S_c = C_P \ln \frac{T}{T_c}$$

The total change in entropy is

$$\Delta S = \Delta S_h + \Delta S_c$$

$$\boxed{\Delta S = C_P \ln \frac{T}{T_h} + C_P \ln \frac{T}{T_c}}$$

$$\boxed{\Delta S = C_P \left(\ln \frac{T}{T_h} + \ln \frac{T}{T_c} \right)}$$

PROBLEMS

1. A 50 g mass of Cu at a temperature of 393 K is placed in a contact with a 100g mass of copper at a temperature of 303K in a thermally insulated container. Calculate q and ΔS_{total} for the reversible process. Use a value of 0.418 4 J g^{-1} K^{-1} for the specific heat capacity of Cu.

Soln. We have 50 g copper at 393 K and 100g copper at 303 K. The temperature of teh two bodies when they have come to thermal equilibrium can be calculated as follows.

Heat gain = heat loss

$$m_1 C_P (\Delta T_1) = m_2 C_P (\Delta T_2) \text{ i.e. } m_1 \Delta T_1 = m_2 \Delta T_2$$

Therefore,

$$(100\ g)(T - 303K) = (50g)(393\ K - T)$$

T = 333K

Thus, $$\Delta S_h = nC_P \ln \frac{T}{T_h}$$

$$= \left(\frac{50\ g}{63\ g\ mol^{-1}} \right) \left\{ \left(0.4184\ J\ g^{-1} K^{-1} \right) \left(63\ g\ mol^{-1} \right) \right\} \times 2.303 \log \left(\frac{333K}{393K} \right)$$

$$= -3.466\ JK^{-1}$$

$$\Delta S_c = nC_P \ln \frac{T}{T_c}$$

$$= \left(\frac{100g}{63\ g\ mol^{-1}} \right) \left\{ \left(0.4184\ J\ g^{-1} K^{-1} \right) \left(63\ g\ mol^{-1} \right) \right\} \times 2.303 \log \left(\frac{333K}{303K} \right)$$

$$= 3.951\ JK^{-1}$$

And $\Delta S_{total} = \Delta S_c + \Delta S_b = (3.951 - 3.466)\, JK^{-1} = 0.485\, JK^{-1}$

2. 5g ice at 200K is added to 30g water at 300K in thermally insulated container. What is the final temperatures? Given : ΔH_{fusion} of ice at 200K = 300 J g^{-1} and average specific heat capacity of liquid water = 4 J $K^{-1}g^{-1}$.
(a) 239 K (b) 380 K (c) 429 K (d) 129K

Soln. Heat required to convert 5g of ice at 200K to 5 g water at 200K

$$= (5g)(300J\ g^{-1}) = 1500\ J$$

Final temperature after mixing.

Heat gained by ice = heat lost by hot water

$$(5g)(300\ Jg^{-1}) + (5g)(4JK^{-1}g^{-1})(T - 200K) = (30g)(4JK^{-1}g^{-1})(300K - T)$$

$$\Rightarrow \quad 1500J + (20J)\left(\frac{T}{K} - 200\right) = (120J)\left(300 - \frac{T}{K}\right)$$

$$\Rightarrow \quad 1500J + 20\ TJK^{-1} - 4000J = 36000J - 120JK^{-1}$$

$$\Rightarrow \quad 140TJK^{-1} = 33500J \quad \Rightarrow \quad T = \frac{33500\ J}{140\ K^{-1}J} \quad \Rightarrow \quad T = 239K$$

Correct option is (a)

Entropy of Mixture of Ideal Gases :

For one mole of an ideal gas,

$$dS = C_V \frac{dT}{T} + R\frac{dV}{V} \qquad \text{... (i)}$$

Integrating equation (i), assuming that C_V remains constant for an ideal gas, we have

$$S = C_V \ln T + R \ln V + S_0 \qquad \text{... (ii)}$$

where S_0 is the integration constant.

We know that, $C_P - C_V = R$ and $V = \frac{RT}{P}$, we get

$$S = C_P \ln T - R \ln P + R \ln R + S_0 \qquad \text{... (iii)}$$

$$= C_P \ln T - R \ln P + S_0' \qquad \text{... (iv)}$$

where, $S_0'(= R \ln R + S_0)$ is another constant.

If n_1, n_2, n_3, etc. are the numbers of moles of various gases present in the mixture and p_1, p_2, p_3, etc. are their partial pressures, then, the entropy of the mixture is given by

$$S = n_1(C_P \ln T - R \ln p_1 + S_0') + n_2(C_P \ln T - R \ln p_2 + S_0') + n_3(C_P \ln T + R \ln p + S_0).....$$

$$= \Sigma n(C_P \ln T - R \ln p + S_0') \qquad \text{... (v)}$$

The partial pressure (p) of an ideal gas is given by the expression,

$$p = xP \qquad \text{... (vi)}$$

where, x is the mole fraction of that particular gas in the mixture and P is the total pressure.
Substituting p by xp in equation (v), we have

$$S = \Sigma n(C_p \ln T - R \ln P - R \ln x + S_0') \qquad \text{... (vii)}$$

Equation (vii) is known as the entropy of a mixture of ideal gas.

Entropy of Mixing : Entropy of mixing is defined as the difference between the entropy of the mixing of gases and the sum of the entropies of the separate gases, each at a pressure P, Thus,

$$\Delta S_{mix} = \Sigma n\left(C_p \ln T - R\ln P - R\ln x + S_0'\right) - \Sigma n\left(C_p \ln T - R\ln P + S_0'\right)$$

$$\Delta S_{mix} = -R\,\Sigma n \ln x = -R\left(n_1 \ln x_1 + n_2 \ln x_2 + n_3 \ln x_3 + ...\right)$$

$$\Delta S_{mix} = -R\,\Sigma n_i \ln x_i$$

where, n_i = number of moles of ith gas.

and x_i = number of mole fraction of ith gas

$$x_i = \frac{n_i}{\Sigma n_i}$$

$$\Rightarrow \quad \Delta S = -2.303R\left[n_1 \log x_1 + n_2 \log x_2\right]$$

$$\Rightarrow \quad \boxed{\Delta S = -2.303R\left[n_1 \log \frac{n_1}{n_1+n_2} + n_2 \log \frac{n_2}{n_1+n_2}\right]}$$

Or, $$\boxed{\Delta S = R\left[n_1 \ln \frac{n_1}{n_1+n_2} + n_2 \ln \frac{n_2}{n_1+n_2}\right]}$$

SOLVED PROBLEMS

1. Assuming that there is no chemical reaction, the change in entropy when 2 moles of N_2, 3 moles of H_2 and 2 moles of HN_3 are mixed at constant temperature is **[GATE 2002]**

(a) $-62.79\ JK^{-1}$ (b) $62.79\ JK^{-1}$ (c) $125.58\ JK^{-1}$ (d) $-125.58\ JK^{-1}$

Soln. Given, $n_1 = 2, n_2 = 3$ and $n_3 = 2$

The mole fraction are

$$x_1 = \frac{n_1}{n_1+n_2+n_3} = \frac{2}{2+3+2} = \frac{2}{7}$$

$$x_2 = \frac{n_2}{n_1+n_2+n_3} = \frac{3}{2+3+2} = \frac{3}{7}$$

and $$x_3 = \frac{n_3}{n_1+n_2+n_3} = \frac{2}{2+3+2} = \frac{2}{7}$$

Therefore, entropy of mixing,

$$\Delta S_{mix} = -2.303R\left[n_1 \log x_1 + n_2 \log x_2 + n_3 \log x_3\right]$$

$$= -2.303 \times 8.314\left[2\log\frac{2}{7} + 3\log\frac{3}{7} + 2\log\frac{2}{7}\right]$$

$$= -19.147 \times \left[-2\times 0.54 - 1.102 - 2\times 0.54\right]$$

$$= -19.147 \times \left[-1.08 - 1.102 - 1.08\right] = -19.147 \times -3262 = 63\ JK^{-1}$$

Correct option is (b)

2. The entropy of mixing of 10 moles of helium and 10 moles of oxygen at constant temperature and pressure, assuming both to be ideal gases, is **[GATE 2007]**

(a) $115.3\ JK^{-1}$ (b) $5.8\ JK^{-1}$ (c) $382.9\ JK^{-1}$ (d) $230.6\ JK^{-1}$

Soln. Given, $n_1 = 10\ moles$ and $n_2 = 10\ moles$

The mole fractions are,

$$\therefore \quad x_1 = \frac{n_1}{n_1+n_2} = \frac{10}{10+10} = \frac{1}{2}$$

And $$x_2 = \frac{n_2}{n_1+n_2} = \frac{10}{10+10} = \frac{1}{2}$$

$$\Rightarrow \quad \Delta S_{mix} = -2.303R\left[\Sigma n_i \log x_i\right]$$

$$\Rightarrow \quad \Delta S_{mix} = -2.303R\left[n_1 \log x_1 + n_2 \log x_2\right]$$

$$= -2.303\times 8.314\left[10\log\frac{1}{2} + 10\log\frac{1}{2}\right]$$

$$= -2.303\times 8.314\times 20\times(-0.3010) = 115.3\ JK^{-1}$$

Correct option is (a)

3. 1 mol of CO_2, 1 mol of N_2 and 2 mol of O_2 were mixed at 300 K. The entropy of mixing is

(a) 6 R ℓn2 (b) 8 R ℓn2 (c) $\frac{8\ R\ \ell n2}{300}$ (d) 16R ℓn 2 **[NET Dec. 2011]**

Soln. Given, $n_1 = 1, n_2 = 1, n_3 = 2$

Mole fractions are,

$$x_1 = \frac{n_1}{n_1+n_2+n_3} = \frac{1}{1+1+2} = \frac{1}{4}$$

$$x_2 = \frac{n_2}{n_1+n_2+n_3} = \frac{1}{1+1+2} = \frac{1}{4}$$

And $$x_3 = \frac{n_3}{n_1+n_2+n_3} = \frac{2}{1+1+2} = \frac{2}{4} = \frac{1}{2}$$

$$\Delta S_{mix} = R\left[n_1 \ln x_1 + n_2 \ln x_2 + n_3 \ln x_3\right]$$

$$= -R\left[1\times\ln\frac{1}{4} + 1\times\ln\frac{1}{4} + 2\times\ln\frac{1}{2}\right]$$

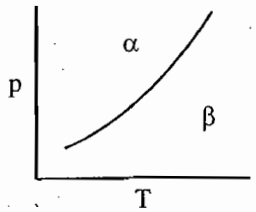
$$= -R\left[2\ln\frac{1}{2} + 2\ln\frac{1}{2} + 2\ln\frac{1}{2}\right] = -6R\left[\ln\frac{1}{2}\right] = 6R\ln 2$$

Correct option is (a)

Clapeyron and Clausius-Clapeyron Equations

The Clapeyron Equation:

In a one-component phase diagram the lines separating the phases (for example, solid from liquid, liquid from vapor, and so on) are not arbitrary, they are determined by the principles of thermodynamics and equilibrium. Thermodynamics provides an equation for each line which gives pressure, p, as a function of temperature T, in other words an equation of the form $p = p(T)$. It is now our task to find the form of the function $p(T)$. The diagram below is a portion of a hypothetical phase diagram and the phase line on this diagram separates α and β. In other words, the phases α and β are in equilibrium with each other at any and all points on the line.



Phase transitions occur at constant temperature and pressure at the points on this line. Consider the phase transition.

$$\alpha \longrightarrow \beta \qquad \ldots (1)$$

Since the α and β phases are in equilibrium with each other at any point on the line we know that the line we know that the change in the Gibbs free energy for the transition given by equation (1) is zero everywhere on the $\alpha - \beta$ phase line. That is,

$$\Delta G = 0 \qquad \ldots (2)$$

We already know that for any process at constant temperature it must be true that

$$\Delta G = \Delta H - T\Delta S \qquad \ldots (3)$$

From equation (2) and equation (3), we get

$$\Delta S = \frac{\Delta H}{T} \qquad \ldots (4)$$

For a phase transition,
The various quantities appearing in these equations are defined as usual by

$$\Delta G = G_\beta - G_\alpha \qquad \ldots (5)$$

$$\Delta S = S_\beta - S_\alpha \qquad \ldots (6)$$

$$\Delta H = H_\beta - H_\alpha \qquad \ldots (7)$$

We will also define ΔV the same way,

$$\Delta V = V_\beta - V_\alpha \qquad \ldots (8)$$

As we have already said, $\Delta G = 0$ alog the $\alpha - \beta$ phase line. That is, ΔG is contant along the line and it is being held constant at the particular value of zero. We want the slope of the line. Therefore, the derivative we want is, $\left(\frac{\partial P}{\partial T}\right)_{\Delta G}$. We can write this derivative in terms of quantities we know using the cyclic rule (Euler's chain relation) as,

$$\left(\frac{\partial P}{\partial T}\right)_{\Delta G} = -\frac{\left(\frac{\partial \Delta G}{\partial T}\right)_p}{\left(\frac{\partial \Delta G}{\partial P}\right)_T} \qquad \ldots (9)$$

We know that from $dG = -SdT + Vdp$, *or* $d\Delta G = -\Delta S dT + \Delta V dp$, that

$$\left(\frac{\partial \Delta G}{\partial T}\right)_p = -\Delta S \qquad \ldots (10)$$

And $$\left(\frac{\partial \Delta G}{\partial T}\right)_T = \Delta V \qquad \ldots (11)$$

Using equation (10) and equation (9), we get

$$\boxed{\left(\frac{\partial P}{\partial T}\right)_{\Delta G} = \frac{\Delta S}{\Delta V}} \qquad \ldots (12)$$

Equation (12) is the Clapeyron equation.
The Clapeyron equation is thermodynamically exact. It contains no approximations. There is another version of the Clapeyron equation which we obtain by inserting equation (4) for ΔS into equation (12).

$$\left(\frac{\partial P}{\partial T}\right)_{\Delta G} = \frac{\Delta H}{T\Delta V} \qquad \ldots (13)$$

Equation (13) is useful when we want to integrate dP to find P as a function of T. The integration of equation (12) or (13) is easiest if we can make the approximation that either ΔS or ΔH is reasonably constant over the temperature range. However, ΔH usually varies more slowly with temperature than does ΔS, so that the approximation is better when we integrate equtaion (13). Prepare equation (13) for integration.

$$dP = \frac{\Delta H}{T\Delta V} dT \qquad \ldots (14)$$

To integrate equation (14) we must know how ΔH and ΔV depend on temperature. We have already said that ΔH can be regarded as approximately constant, but what about ΔV ? ΔV is certainly not even near constant if one of the components of the phase transition is a gas, but if the transition is solid $\rightarrow$ solid or solid $\rightarrow$ liquid we can approximate ΔV as a cosntant also. Then equation (14) integrates to,

$$P_2 - P_1 = \frac{\Delta H}{\Delta V} \ln \frac{T_2}{T_1} \qquad \ldots (15)$$

If we let T_2 and P_2 range over the phase line and call them T and P, respectively, we can write pressure as a function of temperature for a solid $\rightarrow$ solid or solid $\rightarrow$ liquid phase transition line as follows.

$$P_2 = P_1 + \frac{\Delta H}{\Delta V} \ln \frac{T}{T_1} \qquad \ldots (16)$$

The Clausius-Clapeyron Equation:

Equation (12) and (13) are exact and are valid for all types of phase transitions, solid $\rightarrow$ liquid, solid $\rightarrow$ gas, liquid $\rightarrow$ gas, and so on. However, for solid $\rightarrow$ gas and liquid $\rightarrow$ gas phase transitions we can make two approximations which will give us a very useful equation called the Clausius-Clapeyron equation. The first approximation comes from noting that the volume of a given amount of gas is much larger that the volume of an equivalent amount of solid or liquid. This being true, we can approximate ΔV by the volume of the gas. That is,

$$\Delta V = V_{gas} - V_{liquid} \approx V_{gas} \qquad \ldots (17)$$

Or, $$\Delta V = V_{gas} - V_{solid} \approx V_{gas} \qquad \ldots (18)$$

In the second approximation we replace V_{gas} by the volume the gas would have if it were ideal. That is, we set $V_{gas} = \frac{nRT}{P}$. With these two approximation equation (13) becomes

$$\left(\frac{\partial P}{\partial T}\right)_{\Delta G} = \frac{\Delta H}{T\frac{nRT}{P}} = \frac{\Delta H}{R}\frac{P}{T^2} \qquad \ldots (19)$$

where the bar over the enthalpy, H means that it is the enthalpy per mole. Equation (19) is known as the Clausine-Claperyron equation.

We should emphasize that equation (19) is not exact (because it contains two approximately) and it only applies when one of the phases in the phase transition is a gas. Equation (19) can be prepared for integration as follows.

$$\frac{dP}{P} = \frac{\Delta H}{R}\frac{dT}{T^2} \qquad \ldots (20)$$

Equation (20) can be integrated if we know how ΔH changes with temperature or, as we will now do, if we regard ΔH as approximately constant. With the ΔH regarded as constant equation (20) integrates to

$$\boxed{\ln \frac{P_2}{P_1} = -\frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)} \qquad \ldots (21)$$

Equation (21) is the integrated form of the Clausius-Clapeyron equation.

If we want pressure as a function of temperature we can let the point (P_2, T_2) range over the phase line and call it simply (P, T) and then take the antilog of both sides.

$$\boxed{P = P_1 e^{-\frac{\Delta H}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)}} \quad \ldots(22)$$

Notice that if we know two points on the curve we can solve for ΔH, or if we know one point on the curve and ΔH we can solve for any other point or even get the entire curve. Equation (22) is very useful for estimating vapor pressures at various temperatures when ΔH and the vapor pressure at one temperature are known.

Application of Clausius-Clapeyron Equation:

(1) Effect of pressure on boiling point : For $liquid \rightleftharpoons vapour$

Since we know that,

$$\frac{dP}{dT} = \frac{\Delta H_v}{T(V_v - V_\ell)}$$

If $V_v >> V_\ell$, then $\frac{dP}{dT} = (+)\text{ve}$

When pressure increases then dP is positive and if dT is positive so boiling point increase.

If $V_\ell >> V_v$. So, $\frac{dP}{dT} = (-)\text{ve}$

When pressure decreases then dP is negative and if dT is negative. So, boiling point is decreases.

(2) Effect of pressure on melting point :

For fusion, $solid \rightleftharpoons liquid$

Since, we know that

$$\frac{dP}{dT} = \frac{\Delta H_f}{\pi_f (V_\ell - V_s)}$$

If $V_s >> V_\ell$ (e.g. : ice, gallium, bismuthese)

$$\frac{dP}{dT} = (-)ve$$

When pressure increases then dP is negative. So, melting point decreases.

And if $V_\ell >> V_s$ (e.g. wax, sulphur etc.)

$$\frac{dP}{dT} - (+)ve$$

When dP is positive and dT is positive then boiling point increases.

SOLVED PROBLEMS

1. The specific volume of liquid water is 1.001 mLg^{-1} and that of ice is 1.0907 $mL\ g^{-1}$ at 0°C. If the heat of fusion of ice at this temperature is 333.88 $J\ g^{-1}$, the rate of change of melting point of ice with pressure of deg atm^{-1} will be **[GATE 2007]**

(a) – 0.0075 (b) 0.0075 (c) 0.075 (d) –0.075

Soln. Given, $V_\ell = 1.001\ mLg^{-1}$, $V_s = 1.0907\ mLg^{-1}$

Therefore, the rate of change of melting point of ice with pressure is $\frac{dT}{dP}$

Since we know that,

$$\frac{dP}{dT}=\frac{\Delta H}{T\Delta V}=\frac{\Delta H}{T\left(V_\ell - V_s\right)}$$

Or, $$\frac{dT}{dP}=\frac{T\left(V_\ell - V_s\right)}{\Delta H}$$

Or, $$\frac{dT}{dT}=\frac{273K\left(1.001\ mLg^{-1}-1.0907\ mLg^{-1}\right)}{333.88\ J\ g^{-1}}$$

Or, $$\frac{dT}{dP}=\frac{-24.7881\ mLg^{-1}K}{333.88\ Jg^{-1}}=-0.0733$$

Or, $$\frac{dT}{dP}=-0.073\ \text{deg}\ atm^{-1}$$

Correct option is (d)

2. For the liquid $\rightleftharpoons$ vapour equilibrium of a substance $\frac{dP}{dT}$ at 1 bar and 400 K is 8×10^{-3} bar K^{-1}. If the molar volume in the vapour form is 200 L mol^{-1} and the molar volume in the liquid form is negligible, the molar enthalpy of vapourisation is $(1.0\ \text{bar L}=100\ \text{J})$ **[NET Dec. 2011]**

(a) 640 kJ mol^{-1} (b) 100 kJ mol^{-1} (c) 80 kJ mol^{-1} (d) 64 kJ mol^{-1}

Soln. Given, $\frac{dP}{dT}=8\times10^{-3}\ bar\ k^{-1}, T=400K, V_v=200\ L\ mol^{-1}, V_\ell=0, \Delta H_v=?$

Since, we know that,

$$\frac{dP}{dT}=\frac{\Delta H_v}{T\left(V_v - V_\ell\right)}$$

$$\Rightarrow \quad 8\times10^{-3}\frac{bar}{k}=\frac{\Delta H_v}{400k\left(200\frac{L}{mol}-0\right)}$$

$$\Rightarrow \quad \Delta H_v=8\times10^{-3}\frac{bar}{k}\times400k\times200\frac{L}{mol}$$

$$\Rightarrow \quad \Delta H_v=640\frac{bar\ L}{mole}$$

$$\Rightarrow \quad \Delta H_v=640\times100\frac{J}{mol}$$

$$\Rightarrow \quad \Delta H_v=64000\ J\ mol^{-1}$$

$$\Rightarrow \quad \Delta H_v=64\ kJ\ mol^{-1}$$

So, correct option is (d)

3. The vapour pressure of decane is 10 torr at 55.7°C and 40 torr at 150.6°C. The ΔS_{vap} at 100°C is

(a) 12 J K^{-1} (b) 24 J K^{-1} (c) 1.2 J K^{-1} (d) 2.4 J K^{-1}

Soln. Given, $P_1=10\ torr, T_1=273+55.7=328.7\ K$

$$P_2=400\ torr, T_2=273+150.6=423.6\ K$$

Since we know that,

$$\log\frac{P_2}{P_1}=\frac{\Delta H_v}{2.303R}\left[\frac{T_2-T_1}{T_1T_2}\right]$$

$$\log\frac{400}{10}=\frac{\Delta H_v}{2.303\times8.314}\left[\frac{423.6-328.7}{423.6\times328.7}\right]$$

$$\log 40=\frac{\Delta H_v[94.9]}{2.303\times139237.32}\Rightarrow\Delta H_v=4504\ joule$$

And $\Delta S_{vap}=\frac{\Delta H_v}{T}=\frac{4504J}{373K}=12.075\ JK^{-1}$

Correct option is (a)

4. Calculate change in temp of boiling water when the pressure is increased by 27.12mm of Hg. The normal boiling point of water at 1atm is 100°C.

Given, Latent heat of steam = 537cal/g and specific volume of steam = 1674C.C

(a) 1K (b) 2K (c) 3K (d) 4K

Soln : From clausius-clapeyron Equation, we have

$$\frac{dP}{dT}=\frac{\Delta H}{\Delta V}\left(\frac{1}{T}\right)\Rightarrow\frac{dP}{dT}=\frac{\Delta H}{(V_2-V_1)}\left(\frac{1}{T}\right)$$

$$\Rightarrow\quad dT=\frac{(V_2-V_1)}{\Delta H}\times T\times dP \qquad \ldots(i)$$

Here, dP= 27.12mm of Hg

$$\Rightarrow\quad dP=\frac{27.12}{760}\text{ atm}\qquad[\because\ 1\text{atm}=760\text{ mm of Hg}]$$

$$\Rightarrow\quad dP=\frac{27.12}{760}\times1.01\times10^5\text{N/m}^2$$

$$\Rightarrow\quad dP=0.036041\times10^5\text{N/m}^2 \qquad \ldots(ii)$$

$$\Delta H=1\text{g}\times537\frac{\text{cal}}{\text{g}}=537\text{cal}=537\times4.18\text{J}$$

$$\Rightarrow\quad \Delta H=2244.66\text{J} \qquad \ldots(iii)$$

$$V_1=1.\text{c.c}=10^{-6}\ \text{m}^3\Rightarrow V_2=1674\text{c.c}=1674\times10^{-6}\ \text{m}^3$$

$$\Rightarrow\quad \Delta V=V_2-V_1=1673\times10^{-6}\text{m}^3 \qquad \ldots(iv)$$

$$T=100°\text{C}=373\text{K} \qquad \ldots(v)$$

And dT= ?

Now making substitution from the equation (ii), (iii), (iv) and (v) in (1), we get

$$dT=\frac{1673\times10^{-6}m^3}{2244.66\text{J}}\times373\text{K}\times0.036041\times10^5\frac{\text{N}}{m^2}$$

$$\Rightarrow \quad dT = \frac{2249.0629}{2244.66}\frac{(N-m)}{J}K \Rightarrow dT = 1K$$

Correct option is (a)

5. When lead is melt at atmospheric pressure (The melting point is 600K), the density decreases from 11.01 to 10.65g/C.C and the latent heat of fusion is 24.5J/g. What is the melting point at a pressure of 100 atmosphere.

(a) 800K (b) 100 K (c) 200K (d) 600K

Soln : From clausius-clapeyron equation, we have

$$\frac{dP}{dT} = \frac{\Delta H}{\Delta V}\left(\frac{1}{T}\right) \Rightarrow \frac{dP}{dT} = \frac{\Delta H}{(V_2 - V_1)}\left(\frac{1}{T}\right)$$

$$\Rightarrow \quad dT = \frac{(V_2 - V_1)}{\Delta H} \times T \times dP \qquad \ldots (i)$$

Here, $dP = (100 - 1)atm = 99atm = 99 \times 1.01 \times 10^5\ N/m^2$

$$\Rightarrow \quad dP = 99.99 \times 10^5 N/m^2 \qquad \ldots (ii)$$

$$\Delta H = 1g \times \frac{24.5J}{g} = 24.5J \qquad \ldots (iii)$$

$$V_1 = \frac{m_1}{d_1} = \frac{1g\ c.c}{11.01g} = \frac{1}{11.01} \times 10^{-6} m^3 \Rightarrow V_1 = 0.090 \times 10^{-6} m^3$$

$$V_2 = \frac{m_2}{d_2} = \frac{1g\ c.c}{10.65g} = \frac{1}{10.65} \times 10^{-6} m^3 \Rightarrow V_2 = 0.09389 \times 10^{-6}\ m^3$$

$$\therefore \quad \Delta V = V_2 - V_1 = (0.09389 - 0.09082) \times 10^{-6} m^3$$

$$\Delta V = 0.00307 \times 10^{-6} m^3 \qquad \ldots (iv)$$

$$T = 600K \qquad \ldots (v)$$

And $$dT = \frac{0.00307 \times 10^{-6} m^3}{24.5J} \times 600K \times 99.99 \times 10^5 \frac{N}{m^2}$$

$$\Rightarrow \quad dT = \frac{18.419}{24.5}\frac{(N-m)}{J}K$$

$$\Rightarrow \quad dT = 0.75K$$

Therefore, at melting point,

$$100\ atm = (600 + 0.75)K = 600.75\ K$$

Correct option is (d)

6. At what pressure will ice melt at – 1°C assuming that ΔH_f is independent of pressure and $\Delta H_f = 6.0095$ KJ/ mol. [Given, $d_{H_2O} = 0.9998$ g/c.c and $d_{ice} = 0.9170$ g/c.c].

(a) 175 atm (b) 160 atm (c) 135 atm (d) 200 atm

Soln: From clausius clapeyrom equation

$$\log\frac{P_2}{P_1} = \frac{\Delta H_f}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad \ldots (i)$$

$$\Rightarrow \quad P_2 - 1\text{atm} = \frac{\Delta H_f}{\Delta V} \times 2.303 \log_{10}\left(\frac{T_2}{T_1}\right) \qquad \text{... (ii)}$$

Given, $\Delta H_f = 6.0095 \times 10^3$ J/mol ... (iii)

The molar mass of water = 18 g/mol

$= 18 \times 10^{-3}$ Kg/mol

$$V_1 = \frac{m_{ice}}{d_{ice}} = \frac{\frac{18\times10^{-3}\,kg.mol^{-1}}{0.9170\times10^{-3}\,kg}}{10^{-6}\,m^2} = \frac{18\times10^{-6}}{0.9170}\,m^3 mol^{-1}$$

$$\Rightarrow \quad V_2 = \frac{m_{H_2O}}{d_{H_2O}} = \frac{\frac{18.10^{-3}\,kg.mol^{-1}}{0.9998\times10^{-3}\,kg}}{10^{-6}\,m^3} = \frac{18\times10^{-6}}{0.9998}\,m^3 mol^{-1}$$

$$\Rightarrow \quad V_2 = 18.00 \times 10^{-6}\ m^3 mol^{-1}$$

$$\Rightarrow \quad \Delta V = V_2 - V_1 = (18.00 - 19.62) \times 10^{-6}\ m^3\ mol^{-1}$$

$$\Rightarrow \quad \Delta V = -1.629 \times 10^{-6}\ m^3\ mol^{-1} \qquad \text{... (iv)}$$

$T_1 = 0°C = 273K$

$T_2 = 1°C = 272K$

$$\log_{10}\left(\frac{T_2}{T_1}\right) = \log_{10}\left(\frac{272K}{273K}\right) = \log_{10}(0.996)$$

$$\Rightarrow \quad \log_{10}\left(\frac{T_2}{T_1}\right) = -0.0015 \qquad \text{... (v)}$$

Now making substitution from the equation (iii), (iv) and (v) in (ii) we get

$$P_2 - 1\text{ atm} = \frac{6.0095\times10^3\,\text{Jmol}^{-1} \times 2.303 \times [-0.0015]}{-1.629\,m^3 mol^{-1} \times 10^{-6}}$$

$$\Rightarrow \quad P_2 - 1\text{ atm} = \frac{0.022\times10^9}{1.629}\frac{\text{J}}{\text{m}^3}$$

$$\Rightarrow \quad P_2 - 1\text{atm} = \frac{0.013\times10^9}{m^3} \times \frac{1}{1.01\times10^5}\,atm\,m^2$$

$$\left[\begin{array}{l} \therefore 1atm = 1.0\times10^5\,\frac{N}{m^2}\times\frac{m}{m} \\ 1atm.m^3 = 1.01\times10^5\,Nm, \\ \Rightarrow 1atm.m^3 = 1.01\times10^5\,\text{J} \end{array}\right]$$

$$\Rightarrow \quad P_2 - 1\text{ atm} = 0.01343 \times 10^4\text{ atm}$$

$$\Rightarrow \quad P_2 = 1\text{atm} + 0.01343 \times 10^4\text{ atm};\ P_2 = 1\text{ atm} + 134.3\text{ atm}$$

$$\Rightarrow \quad P_2 = 135.3\text{ atm}$$

Correct option is (c)

PRACTICE SET

1. The ΔS accompanying the evaporation of one mole of water at 100°C, assuming the ΔH_{vap} of water is 540 cal g^{-1} is
(a) 540 calg^{-1} (b) 25 cal k^{-1} mol^{-1} (c) 20 cal k^{-1} mol^{-1} (d) 26.0 cal k^{-1} mol^{-1}

2. A carnot engine converts one-sixth of heat input into work. When the temperature of the sink is reduced by 62°C, its efficiency is doubled. The temperature of the source and the sink respectively
(a) 372K, 310K (b) 372K, 410K (c) 410K, 372K (d) 410K, 310K

3. A carnot engine operates between a source at temperature 300K and a sink at temperature 200 K. Let η be the efficiency of the Carnot engine when the temperatures of both the source and the sink are decreased by the same amount. Then,
(a) $\eta < 1/3$ (b) $\eta > 1/3$ (c) $\eta = 1/3$ (d) $\eta = 1/2$

4. The change in entropy when two mole of ice are heated from –10°C to 10°C
C_p, ice = 37.7 J/k-mole
C_p, l = 75.3 J/k-mole (Heat capacity is independent of temperture)
$$\Delta H_f = 6.01 \frac{kJ}{mole}$$
(a) 52.26 J/K (b) 44.03 J/K (c) 46.84 J/K (d) 49.45 J/K

5. The ΔS for 3 mole of an ideal gas (diatomic) which is heated and compressed from 298K and 1 bar to 398K and 5 bar $\left(C_P = \frac{7}{2}R\right)$
(a) –14.88 J/K (b) 14.88 J/K (c) –4.62 J/K (d) 4.62 J/K

6. Consider the statement
(1) ΔU_{fusion} and ΔH_{fusion} have same vlaue.
(2) The change in enthalpy when 50 litre ethanole initially at 1 bar and 300K is heated to 9 bar nd 400K is 8000J/mole. (If Cp methanol is 80 J/k-mole)
(3) The value of $\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_T$ for 1 mole of ideal gas is $-\frac{V^2}{T^2}$
Correct statement is
(a) 1, 2 (b) 2, 3 (c) 1, 3 (d) 1 only

7. What is ΔA for the process
$$2He(g, 27°C, 1 atm) \rightarrow 2He(g, 27°C, 5 atm)$$
assuming that the process is reversible
(a) 8.029 kJ (b) 802.9 kJ (c) 80.29 kJ (d) 0.8029kJ

8. ΔH^0_{298} for the reaction,
$$C_2H_4O(g) \longrightarrow CH_4(g) + CO(g)$$
is –16.0 kJ. From the given data, evaluate the temperature at which ΔH will be zero.

Substance :	$C_2H_4O(g)$	$CH_4(g)$	$CO(g)$
Cp(J/K mole) :	50	36	30

(a) 1298K (b) 1000K (c) 1298°C (d) 1100°C

9. Choose the correct criterian of spontaneity in term of the properties of the system alone

(a) $(dS)_{T,P} < 0$ (b) $(dS)_{H,P} < 0$ (c) $(dG)_{T,V} < 0$ (d) $(dS)_{U,V} > 0$

10. One mole of Helium is mixed with 2 mole of Neon both at the same temperature and at same pressure if the total volume remains constant than ΔS_{He} and ΔS_{Ne} respectively are

(a) 6.743 J/k, 9.136 J/k (b) 9.136 J/k, 6.743 J/k
(c) 13.486 J/k, 18.272 J/k (d) 6.743, 13.486 J/k

11. 100 gm nitrogen at 298 K are held by a piston under 30 atm pressure. The pressure is suddently released to 10 atm and the expands adiabatically if $(C_V = 20.8\ J/k-mole)$ value of ΔS_{system}, $\Delta S_{surrounding}$, $\Delta S_{universe}$ is:

(a) All are zero because process is adiabatic (b) 2.932 J/k, 0, 2.932 J/k
(c) 10.47 J/k, 0, 10.47 J/k (d) 3.571 J/k, 0, 3.571 J/k

12. The molar heat capacity at constant pressure of $H_2O(g)$ at 1.00 atm is given by

$$C_P = 30.54 + 10.3 \times 10^{-2}\ T$$

The change in entropy when 2.0 mole of water at 1.00 atm. The temperature of $H_2O(g)$ is increased from 300K to 1000 K is:

(a) 87.96 J/k (b) 8.796 J/k (c) 879.6 J/k (d) 0.8796 J/k

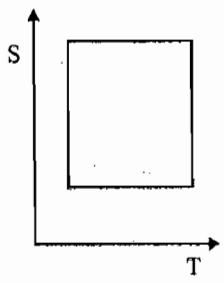
13. Which of the following are the correct criteria for naturally occuring (spontaneous) processes?
(E = internal energy, S = Entropy, G = Gibb's free energy, A = Helmholtz free energy)

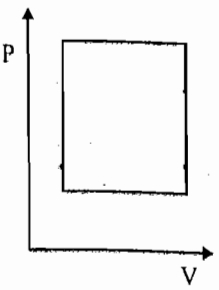
(a) $(\Delta G)_{T,V} \le 0$ (b) $(\Delta A)_{T,P} \le 0$ (c) $(\Delta S)_{E,P} \ge 0$ (d) $(\Delta E)_{S,V} \le 0$

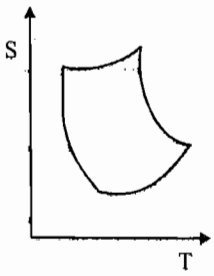
14. For mixing of two ideal gases at 25°C and 1 atm, which one of the following is incorrect?

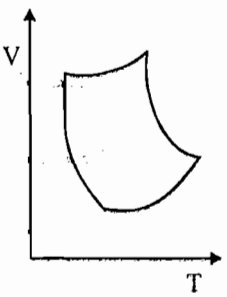
(a) $\Delta T_{mix} = 0$ (b) $\Delta H_{mix} = 0$ (c) $\Delta V_{mix} = 0$ (d) $\Delta S_{mix} = 0$

15. The plot that describes a Carnot cycle is:

(a) 

(b) 

(c) 

(d) 

16. The correct order of ratio of the $\frac{dP}{dT}$ for three phases transformation is:

(a) $\left(\frac{dP}{dt}\right)_{S-L} > \left(\frac{dP}{dt}\right)_{L-g} > \left(\frac{dP}{dt}\right)_{S-g}$ (b) $\left(\frac{dP}{dt}\right)_{L-g} > \left(\frac{dP}{dt}\right)_{S-g} > \left(\frac{dP}{dt}\right)_{S-L}$

(c) $\left(\frac{dP}{dt}\right)_{S-g} > \left(\frac{dP}{dt}\right)_{S-L} > \left(\frac{dP}{dt}\right)_{L-g}$ (d) $\left(\frac{dP}{dt}\right)_{S-L} > \left(\frac{dP}{dt}\right)_{S-g} > \left(\frac{dP}{dt}\right)_{L-g}$

17. If the enthalpy and entropy changes for the following process, $C_6H_6(\ell) \rightarrow C_6H_6(g)$ are respectively, 33.90 $KJmol^{-1}$ and 96.4 $Jmol^{-1}K^{-1}$, the temperature at which the vapour pressure of $C_6H_6(g)$ is 35 Torr will be

(a) 352 K (b) 507 K (c) 278 K (d) 273 K

18. Consider the following statement

I. Entropy of universe is continually increasing.

II. Total entropy change for a reverrisible isothermal cycle is zero.

III. $\Delta S_{mix} = 0$ for ideal gas

IV. Entropy is unavailable work

Correct statement is:

(a) I, II, III, IV (b) I, II, III (c) I, II, IV (d) I, IV

19. For heating in Joule Thomson coefficient which of the following option is true

(a) $\left(\frac{\partial H}{\partial P}\right)_T < 0$ means $T\left(\frac{\partial V}{\partial T}\right)_P < V$

(b) $\left(\frac{\partial H}{\partial P}\right)_T > 0$ means $T\left(\frac{\partial V}{\partial T}\right)_P < V$

(c) $\left(\frac{\partial H}{\partial P}\right)_T < 0$ means $T\left(\frac{\partial V}{\partial T}\right)_P > 0$

(d) $\left(\frac{\partial H}{\partial P}\right)_T > 0$ means $T\left(\frac{\partial V}{\partial T}\right)_P > V$

20. A carnot engine works between the temperature 300K and 400K and takes 6kJ energy. Then what is the work done

(a) 1 kJ (b) 1.5 kJ (c) 2.5 kJ (d) 2.0 kJ

ANSWER KEY					
Questions	1	2	3	4	5
Option	(d)	(a)	(b)	(a)	(a)
Questions	6	7	8	9	10
Option	(a)	(a)	(a)	(d)	(a)
Questions	11	12	13	14	15
Option	(c)	(a)	(d)	(d)	(a)
Questions	16	17	18	19	20
Option	(a)	(c)	(c)	(b)	(b)

Chapter 4

Equilibrium Criteria free Energy Function

Introduction:

This chapter begins with a discussion of mathematical properties of the total differential of a dependent variable. Three extensive state functions with dimensions of energy are introduced: enthalpy, Helmholtz energy, and Gibbs' energy. These functions together with internal energy, are called ***thermodynamics potentials***. Some formal mathematical manipulation of the four thermodynamic potentials are described that lead to expressions for heat capacities surface work and criteria for spontaneity in closed system.

Free Energy Functions

In thermodynamics, two new functions have been introduced to explain various physical and chemical processes occuring at constant temperature and at constant pressure. These functions are called free energies or free energy functions. These are –

(a) Helmholtz free energy or work function

(b) Gibb's free energy or Gibb's potential.

Helmholtz's free energy (A) : A = U - TS :

Helmholtz free energy functional (A) is some time called ***work function*** or ***maximum work*** content of the system. At a constant temperature, the maximum work obtainable from a system is at the expanse of decrease in the Helmholtz free energy of the sytsem.

We know that, $dS \geq \frac{dq}{T}$

And $dq = dU + PdV$

$\therefore \quad dS \geq \frac{dU + PdV}{T} \Rightarrow TdS \geq dU + PdV$

$dU + PdV - TdS \leq 0$

If volume is constant i.e. $dV = 0$

$\therefore \quad (dU - TdS)_V \leq 0$

If temperature of the system is also constant

$\therefore \quad (\partial U - TS)_{V,T} \leq 0$

The quantity $(U - TS)$ is referred to as Helmholtz free energy and is represented by **A**

$\therefore \quad \boxed{A = U - TS}$

Therefore, for a given process

$$(\partial A)_{V,T} \leq 0$$

A is an extensive property and state function. Hence, dA is an exact differential for isotehrmal process

$$dA = dU - TdS$$

Or, $\boxed{\Delta A = \Delta U - T\Delta S}$

Significane of Helmholtz free energy:

Since we know that,

$$\Delta A = \Delta U - T\Delta S$$

Or, $$\Delta A = \Delta U - T\frac{q_{rev}}{T} \qquad \left[\because \Delta S_{rev} = \frac{q_{rev}}{T}\right]$$

Or, $$\Delta A = \Delta U - q_{rev}$$

But from first law of the thermodynamics, $\Delta U = q + w$

$$w_{rev} = \Delta U - q_{rev}$$

In case of work is done by the sytem, then sign is negative.

$$-w_{rev} = \Delta U - q_{rev}$$

$$-w_{rev} = \Delta A$$

Or, $$\boxed{-\Delta A = w_{rev}}$$

where w_{rev} represents maximum useful work done during the reversible process. Hence, decreases in Helmholtz free energy gives the maximum work obtained from the system.

Variation of A with temperature and volume:

$$\because \quad A = U - TS$$

$$\therefore \quad dA = dU - TdS - SdT \qquad \ldots (1)$$

From first law

$$dq = dU + PdV$$

From second law

$$dq = TdS$$

Therefore, equation (1) becomes

$$\boxed{dA = -PdV - SdT}$$

$\Rightarrow$ At constant volume, dV=0

$$\therefore \quad \left(\frac{\partial A}{\partial T}\right)_V = -S$$

$\Rightarrow$ At constant temperature, dT=0

$$\therefore \quad \left(\frac{\partial A}{\partial V}\right)_T = -P$$

Note: $\boxed{(\Delta A)_{\text{ideal gas}} > (\Delta A)_{\text{Vander waal gas}}}$

Gibb's free energy functions (G): G = H – TS :

It is that thermodynamics quantity of a system the decrease in which value during a process is equalto the useful work done other than work of expansions.

Since, we know that, $dS \geq \frac{dq}{T}$

$$dS \geq \frac{dU + PdV}{T}$$

$$dU + PdV - TdS \leq 0 \qquad \ldots (1)$$

If P & T are constant, then equation (1) becomes

$$\partial(U + PV - TS)_{P,T} \leq 0 \qquad \ldots (2)$$

The quantity $(U+PV-TS)$ is referred to as the Gibb's free energy & is represented by G. Hence G is defined as.

$$\boxed{G=E+PV-TS} \quad \ldots (3)$$

Since $H=E+PV$

$$\therefore \quad \boxed{G=H-TS} \quad \ldots (4)$$

Therefore, for a given process.

$$(\partial G)_{P,T} \leq 0$$

G is an extensive process and it is a state function because it depends on H, T & S which are all state functions. If dG is exact differential, so

$$\boxed{dG=dH-TdS}$$

or, $$\boxed{\Delta G=\Delta H-T\Delta S}$$

Significance of Gibb's free energy function :

The change in Gibb's free energy is given by

$$\Delta G=\Delta H-T\Delta S$$

Since, we know that

$$\Delta H=\Delta U+P\Delta V$$

$\therefore$ $\Delta G=\Delta H+P\Delta G-T\Delta S$ but $\Delta A=\Delta U-T\Delta S$

$\therefore$ $\Delta G=\Delta A+P\Delta V=-w_{rev}+P\Delta V$

$$-\Delta G=w_{rev}-P\Delta V$$

Hence, the decrease in free energy functions gives the maximum work that can be obtained from a system at constant temperature and pressure.

At constant volume $P\Delta V=0$

Therefore, $-\Delta G=w_{rev}$

or, $-w_{rev}=\Delta G$

or, $\boxed{\Delta G=\Delta A}$

Variation of (G) with temperature and pressure:

$\because$ $G=H-TS$

$$dG=dH-TdS-SdT$$

But $H=U+PV$

$\therefore$ $dH=dU+PdV+VdP$

$\therefore$ $dG=dU+PdV+VdP-TdS-SdT$

$\because$ from first and second law of thermodynamics

$$TdS=dU+PdV$$

$\therefore$ $\boxed{dG=VdP-SdT}$ $\ldots (1)$

$\Rightarrow$ When pressure is constant, $dP=0$, $(dG)_P=-(SdT)_P$

$\therefore$ $\left(\frac{dG}{dT}\right)_P=-S$

When temperature is constant, $dT=0$

$$(dG)_T=(VdP)_T$$

$$\therefore \quad \left(\frac{dG}{dT}\right)_T = V \qquad \ldots (2)$$

Integrating equation (2)

$$\Rightarrow \quad \int_{G_1}^{G_2} dG = \int_{P_1}^{P_2} V dP$$

But for ideal gas, $PV = RT$

$$\Rightarrow \quad \int_{G_1}^{G_2} dG = RT \int_{P_1}^{P_2} \frac{dP}{P}$$

$$\Rightarrow \quad G_2 - G_1 = RT \ell n \frac{P_2}{P_1}$$

$$\boxed{\Delta G = RT \ell n \frac{P_2}{P_1}}$$

For 'n' mole of ideal gas.

$$\boxed{\Delta G = nRT \ln \frac{P_2}{P_1}}$$

For an isothermal process,

$$P_2V_2 = P_1V_1 \quad \text{or} \quad \frac{P_2}{P_1} = \frac{V_1}{V_2}$$

$$\therefore \quad \boxed{\Delta G = 2.303\, nRT \log \frac{V_1}{V_2}}$$

Importance of Gibb's free energy or efficiency of energy Conversion:

Since we know that

$$\Delta G = \Delta H - T\Delta S \Rightarrow \Delta H = \Delta G + T\Delta S$$

$$\text{Efficiency of energy conversion} = \frac{\text{Net useful work obtainable}}{\text{Total energy}} = \frac{\Delta G}{\Delta H} = \frac{\Delta H - T\Delta S}{\Delta H}$$

$$\boxed{\text{Efficiency of energy conservation} = 1 - \frac{T\Delta S}{\Delta H}}$$

Case-I: For spontaneous process, the entropy increases i.e. $\Delta S = +ve$

Therefore, efficiency of energy conversion $\leq 100\%$

Case-II: When the change is at equilibrium, entropy is maximum, then $\Delta S = 0$

Therefore, efficiency of energy conversion = 100%

Calculation of ΔG :

Since we know that

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta H_{(reaction)} = \sum^{Product} n_i \Delta H_f - \sum^{reactant} n_j \Delta H_g$$

$$\Delta S_{(reaction)} = \sum^{product} n_i S - \sum^{reactant} n_j S$$

$\therefore \quad \Delta G_{(reaction)} = \Delta H_{(reaction)} - T\Delta S_{(reaction)}$

Exoergonic and Endoergonic reaction:

The chemical reaction in which free energy decreases $(\Delta G = -ve)$ are called exo-ergonic and the chemical reactions accompanied by increase of free energy i.e. ΔG is positive are known as endo-ergonic.

Standard free energy change.

$$\Delta G^0 = \sum^{product} n_i \Delta G_f^0 - \sum^{reactant} n_j \Delta G_f^0$$

Coupled reaction:

Those biological reaction which are non-spontaneous $(\Delta G = +ve)$, becomes spontaneous when coupled with a reaction whose ΔG is highly negative. So that change of free energy of both the reactions is negative. These pair of reactions are called as coupled reactions.

Biological reactions are generally coupled reaction.

Example : Conversion of Glucose into Glucose -6-phosphate

(i) $Glucose + H_3PO_4 \rightarrow Glucose - 6 - phosphate + H_2O$ $\quad \Delta G^0 = +12.5 \text{ kJ / mole}$

(ii) $ATP + H_2O \rightarrow ADP + H_3PO_4$ $\quad \Delta G^0 = -34.1 \text{ kJ / mole}$

Adding both the reaction, we get coupled reaction is

$Glucose + ATP \rightarrow Glucose - 6 - phosphate + ADP$

$\Delta G^0 = -34.1 + 12.5$

$\Delta G^0 = -12.6 \text{ kJ / mole}$

Thus the conversion of Glucose into Glucose - 6 - phosphate becomes spontaneous.

Enthalpy, Entropy and Free energy changes and the nature of reaction:

ΔH	ΔS	$\Delta G = \Delta H - T\Delta S$	Conclusion
−	+	−	Spontaneous
−	−	[−at low T +at high T]	[spontaneous non-spontaneous]
+	+	[+at low T −at hihg T]	[Non − spontaneous spontaneous]
+	−	+	Non − spontaneous

Gibb's - Helmholtz's equation: (Temperature dependence of free energy).

1. First form of Gibb's - Helmholtz equation:

The change in the free energy with temperature at constant pressure as given by

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \qquad \ldots (1)$$

From the definition of $G(= H - TS)$, we have

$$-S = \frac{G - H}{T} \qquad \ldots (2)$$

Substituting this in equation (2), we get

$$\left(\frac{\partial G}{\partial T}\right)_P = \frac{G - H}{T} \text{ or } G = H + T\left(\frac{\partial G}{\partial T}\right)_P \qquad \ldots (3)$$

In actual practice, one commonly employes the relations which give the variation in ΔG with temperature. Such expressions can be conveneniently written starting from equation (1) with the replacement of G with ΔG and that of S with ΔS.

We have,

$$\left(\frac{\partial(\Delta G)}{\partial T}\right)_P = \Delta S = \frac{\Delta G - \Delta H}{T} \quad \ldots (4)$$

Or,
$$\boxed{\Delta G = \Delta H + T\left(\frac{\partial(\Delta G)}{\partial T}\right)_P}$$

This equation is called Gibbs-Helmholtz equation.

2. Second form of Gibb's Helmholtz's equation:

Variation of Helmholtz's free energy with respect to temperature at constant volume is called second form of Gibb's -Helmholtz's equation.

Since, we know that

$$A = U - TS \quad \Rightarrow \quad \Delta A = \Delta U - T\Delta S \quad \ldots (1)$$

At constant temperature, we get

$$\therefore \quad \left(\frac{\partial \Delta A}{\partial T}\right)_v = \left(\frac{\partial U}{\partial T}\right)_v - \left[\frac{\partial \overset{(I)}{T}\overset{(II)}{(\Delta S)}}{\partial T}\right]_v$$

$$= \left(\frac{\partial U}{\partial T}\right)_v - T\left(\frac{\partial \Delta S}{\partial T}\right)_v - \Delta S\left(\frac{\partial T}{\partial T}\right)_v$$

Since we know that,

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V \text{ and } T\left(\frac{\partial \Delta S}{\partial T}\right)_V = C_V$$

So, putting these values in above equation, we get

$$\left(\frac{\partial \Delta A}{\partial T}\right)_V = C_V - C_V - \Delta S$$

$$\Rightarrow \quad \left(\frac{\partial \Delta A}{\partial T}\right)_V = -\Delta S \Rightarrow \Delta S = -\left(\frac{\partial \Delta A}{\partial T}\right)_V$$

From equation (1), we get

$$\Delta A = \Delta U - T\left[\left(-\frac{\partial \Delta A}{\partial T}\right)_V\right]$$

$$\boxed{\Delta A = \Delta U + T\left(\frac{\partial \Delta A}{\partial T}\right)_V}$$

Temperature dependence of $\Delta G/T$:

Since, we know that at a constant temperature, $\Delta G = \Delta H - T\Delta S$, so that

$$\frac{\Delta G}{T} = \frac{\Delta H - T\Delta S}{T} = \frac{\Delta H}{T} - \Delta S$$

Differentiating $\frac{\Delta G}{T}$ with respect to temperature at constant pressure, we get

$$\left(\frac{\partial(\Delta G/T)}{\partial T}\right)_p = \left(\frac{\partial(\Delta H/T)}{\partial T}\right)_p - \left(\frac{\partial(\Delta S)}{\partial T}\right)_p$$

$$= -\frac{1}{T^2}\Delta H + \frac{1}{T}\left(\frac{\partial(\Delta H)}{\partial T}\right)_p - \left(\frac{\partial(\Delta S)}{\partial T}\right)_p \quad \ldots (1)$$

Since we know that,

$$\left(\frac{\partial(\Delta H)}{\partial T}\right)_p = C_p \text{ and } T\left(\frac{\partial(\Delta S)}{\partial T}\right)_p = C_p$$

Putting this values in equation (1), we get

$$\left\{\frac{\partial(\Delta G/T)}{\partial T}\right\}_p = -\frac{\Delta H}{T^2} + \frac{\Delta C_p}{T} - \frac{\Delta C_p}{T}$$

$$\boxed{\left\{\frac{\partial(\Delta G/T)}{\partial T}\right\}_p = -\frac{\Delta H}{T^2}} \quad \ldots (2)$$

Or, $$\left\{\frac{\partial(\Delta G/T)}{-(1/T^2)\partial T}\right\}_p = \Delta H$$

Since, $d\left(\frac{1}{T}\right) = -\frac{1}{T^2}dT$. So, from above equation, we get

$$\boxed{\Delta H = \left\{\frac{\partial(\Delta G/T)}{\partial(1/T)}\right\}_p}$$

If ΔH is independent of temperature; the plot of $\frac{\Delta G}{T}$ versus $\frac{1}{T}$ will be a straight line with slope equal to ΔH.

If ΔH depends on temperature, then the slope of the plot at $\frac{1}{T}$ gives ΔH at temperature T.

SOLVED PROBLEMS

1. The free energy change (ΔG) accompanying a given process is –85.77 kJ at 25°C and –83.68 kJ at 35°C. Calculate the change in enthalpy (ΔH) for the process at 30°C.

Soln. ΔG at 25°C = –85.77 kJ and at 35°C = –83.68 kJ

$$\therefore \quad \left(\frac{\partial(\Delta G)}{\partial T}\right)_p = \frac{-83.68kJ - (-85.77kJ)}{308K - 298K} = 0.209\ kJ\ K^{-1}$$

ΔG at 30°C may be taken as the average of the values at 25°C and 35°C.

$$\therefore \quad \Delta G \text{ at } 30°C = -\left(\frac{85.77kJ + 83.68kJ}{2}\right) = -84.725kJ$$

$$-84.725kJ = \Delta H + (303K)(0.209kJ\ K^{-1})$$

Hence, $\Delta H = -148.05kJ$

2. For the reaction,

$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g)$, $\Delta G^0_{298K} = -16.45 \text{ kJ mol}^{-1}$ and $\Delta H^0_{298K} = -46.11 \text{ kJ mol}^{-1}$. Estimate the value of ΔG^0_{500K} if ΔH^0 is considered independent of temperature,

Soln. We know that

$$\Delta G^0_T = \Delta H^0 + \frac{T}{T_0}\left(\Delta G^0_{T_0} - \Delta H^0\right)$$

We get,

$$\Delta G^0_T = -46.11 \text{ kJ mol}^{-1} + \left(\frac{500K}{298K}\right)\left(-16.45 \text{ kJ mol}^{-1} + 46.11 \text{ kJ mol}^{-1}\right)$$

$$= 3.66 \text{ kJ mol}^{-1}$$

3. What is the ΔG^0 for the reaction

$$C(\text{graphite}) + 2H_2(g) + N_2(g) + \frac{1}{2}O_2(g) \rightarrow CO(NH_2)_2$$

from the following data

(i) $CO_2(g) + 2NH_3(g) \rightarrow H_2O(g) + CO(NH_2)_2$; $\Delta G^0 = 1.91\ kJ\ mol^{-1}$

(ii) $H_2O(g) \rightarrow H_2(g) + \frac{1}{2}O_2(g)$; $\Delta G^0_2 = 227.44\ kJ\ mol^{-1}$

(iii) $C(\text{graphite}) + O_2(g) \rightarrow CO_2(g)$; $\Delta G^0_3 = -394.38\ kJ\ mol^{-1}$

(iv) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$; $\Delta G^0_4 = -32.43\ kJ\ mol^{-1}$

(a) 197.46 kJ mol^{-1} (b) –197.46 kJ mol^{-1} (c) 157.46 kJ mol^{-1} (d) –157.46 kJ mol^{-1}

Soln. The given reaction is,

$$C(\text{graphite}) + 2H_2(g) + N_2(g) + \frac{1}{2}O_2(g) \rightarrow CO(NH_2)_2$$

The above reaction can be obtained by adding the given reactions. Thus, we have

$$\Delta G^0 = \Delta G^0_1 + \Delta G^0_2 + \Delta G^0_3 + \Delta G^0_4 = -197.46\ kJ\ mol^{-1}$$

Correct option is (b)

4. ΔG^0 at 298K for the following reaction is $-3.202\ MJ\ mol^{-1}$

$$C_6H_6(1)+7\frac{1}{2}O_2(g)\rightarrow 6CO_2(g)+3H_2O(\ell)$$

What is ΔA^0 at 298K.

(a) –3.198 MJ mol^{-1} (b) 3.198 MJ mol^{-1}

(c) 2.188 MJ mol^{-1} (d) –2.188 MJ mol^{-1}

Soln. For this reaction,

$$\Delta v_B = 6-7\frac{1}{2}=-1\frac{1}{2}$$

Now, $\Delta G^0=\Delta A^0+\Delta(PV)=\Delta A^0+(\Delta v_g)RT$

Or, $\Delta A^0=\Delta G^0-(\Delta v_g)RT$

Substituting the given values, we get

$$\Delta A^0=-3.202\times10^6\ J\ mol^{-1}-\{(-1.5)(8.314\ JK^{-1}mol^{-1})(298K)\}$$

$$=-3.202\times10^6\ J\ mol^{-1}+3716.36\ J\ mol^{-1}$$

$$=-3.198\times10^6\ J\ mol^{-1}=-3.198\ MJ\ mol^{-1}$$

Correct option is (a)

5. For an ideal gas undergoing isothermal reversible expansion, ΔG is equal to

(a) ΔU (b) ΔS (c) ΔA (d) ΔT

Soln. The function G and A are given by

$$G=H-TS \text{ and } A=U-TS$$

The function H is given by

$$H=U+PV$$

Substituting this in the function G, we get

$$G=(U+PV)-TS=(U-TS)+PV$$

Or, $G=A+PV$

Thus, for a process

$$\Delta G=\Delta A+\Delta(PV)$$

Now for an isothermal expansion of an ideal gas, we have

$$\Delta(PV)=\Delta(nRT)=0 \text{ as } \Delta T=0$$

So, that $\Delta G=\Delta A$

Correct option is (c)

PRACTICE SET

1. The free energy change (ΔG) for a given process is –79.8 kJ at 20°C and –77.4 kJ at 30°C. What is the change in enthalpy of the process at 25°C
(a) –150.12 kJ (b) 150.12 kJ (c) 101.12 kJ (d) 101.12 kJ

2. Which of the following properties are characteristics of an ideal solution? **[GATE 2015]**
(i) $(\Delta_{max}G)_{T,P}$ is negative (ii) $(\Delta_{max}S)_{T,P}$ is positive
(iii) $(\Delta_{max}V)_{T,P}$ is positive (iv) $(\Delta_{max}H)_{T,P}$ is negative
(a) (i) and (iv) (b) (i) and (ii) (c) (i) and (iii) (d) (iii) and (iv)

3. What is the (ΔG) for the conversion of 3 mol of liquid benzene at 80°C (normal boiling point) to vapour at the same temperature and a pressure of 0.66 bar. Consider the vapour as an ideal gas.
(a) –3.66 kJ mol^{-1} (b) 3.66 kJ mol^{-1} (c) 1.66 kJ mol^{-1} (d) –1.66 kJ mol^{-1}

4. What is the difference between ΔG and ΔA at 20°C for the reaction,
$$H_2(g, 1\text{ atm}) + \frac{1}{2}O_2(g, 1\text{ atm}) = H_2O(\ell)$$
(a) –3.716 kJ mol^{-1} (b) 3.716 kJ mol^{-1} (c) –2.316 kJ mol^{-1} (d) 2.316 kJ mol^{-1}

5. For a certain process, $\Delta G = -50.208$ kJ and $\Delta H = -73.22$ kJ at 400 K. For the process at this temperature $\Delta S = -57.47$ JK^{-1}. What is the value of $\left[\frac{\partial(\Delta G)}{\partial T}\right]_P$
(a) 48.57 JK^{-1} (b) 54.47 JK^{-1} (c) 66.47 JK^{-1} (d) 77.47 JK^{-1}

ANSWER KEY					
Questions	1	2	3	4	5
Option	(a)	(b)	(a)	(a)	(b)

Chapter 5

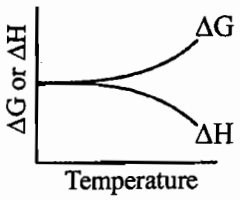
Third Law of Thermodynamics

Introduction:

The first and second law of thermodynamics have led to new concepts of energy content and entropy. The third law, however, does not lead to any new concept. It only places a limitation on the value of the entropy of a crystalline solid. The third law of thermodynamics is state that regarding the properties of system in equilibrium at absolute zero temperature. The entropy of perfect crystal, at absolute zeroth law is exactly equal to zero.

Nernst - Heat Theorem:

W-Nernst in 1906, studid the variation of enthalpy (ΔH) and free energy (ΔG) with decrease of temperature (in figure).



According to Gibbs-Helmholtz equation

$$\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_P \qquad \text{... (i)}$$

at absolute zero, i.e. when $T = 0$, $\Delta G = \Delta H$. However, Nernst observed that as the temperature is lowered towards absolute zero, the value of $\frac{\partial(\Delta G)}{\partial T}$ decrases and then approach zero asymptotically. This means that ΔG and ΔH are not only equal at the absolute zero but the value approach each other asymptotically in the vicinity of the temperature. The result is known as Nernst heat theorem.

$$\lim_{T\to 0}\frac{d(\Delta G)}{dt} = \lim_{T\to 0}\frac{d(\Delta H)}{dT} = 0 \qquad \text{... (ii)}$$

ΔG has been show as greater than ΔH temperature away from the absolute zero.

However, the reverse is also possible because $\frac{d(\Delta G)}{dT}$ can becomes positive or negative.

But we know that

$$\left(\frac{d(\Delta G)}{dT}\right) = -\Delta S \qquad \text{... (iii)}$$

And $$\left(\frac{d(\Delta H)}{dT}\right) = -\Delta C_p \qquad \text{... (iv)}$$

Combining equation (iii) and (iv), we get

$$\lim_{T\to 0}\Delta S = 0 \qquad \text{and} \qquad \lim_{T\to 0}\Delta C_p = 0$$

Since gases do not exist at the absolute zero, this means that the heat theorem is not applicable to gases. Similarly, it has been found to be inapplicable to liquid also.

Problem: The free energy change accompanying a given process –85.77 and –83.68 kJ at 25°C and 35°C, respectively. The change in enthalpy for the process at 30°C is

(a) –148.05 kJ (b) 148.05 kJ (c) 180.05 kJ (c) –180.05kJ

Soln. ΔG at 30°C $= \dfrac{-85.77+(-83.68)}{2} = -84.725\ kJ$

$$\left(\frac{d(\Delta G)}{dT}\right)_P = \frac{-83.68-(85.77)}{308-298} = 0.209\ kJ$$

Since, we know that,

$$\Delta G = \Delta H + T\left(\frac{d(\Delta G)}{dT}\right)_P$$

$$-84.72 = \Delta H + 303\times 0.209$$

$$\Delta H = -148.05\ kJ$$

Correct option is (a)

The Third law of thermodynamics :

The third law of thermodynamics concerns the entropy perfectly-ordered crystal at zero kelvins.

When a chemical reactions or phase transition is studied at low temperatures, and all substance are pure crystals presumed to be perfectly ordered, the entropy change is found to be approach as the temperature approaches zero kelvins.

$$\lim_{T\to 0}\Delta S = 0 \qquad \text{... (i)}$$

(Pure, perfectly-ordered crystals)

Equations (i) is the mathematical statement of the Nernst heat theorem or ***third law of thermodynamics***. It is true in general only if each reactant and product is a pure crystal with identical unit cells arranged in perfect spatial order.

The zero of Entropy : "If the entropy of each element in some crystalline state be taken as zero at the absolute zero of the temperature : every substance has a finite positive entropy may becomes zero and does so become in the case of perfect crystalline substances."

According to this principle, every substance (element or compound) in a pure, perfectly-orderd crystal at 0K, at any pressure has a molar entropy of zero

$$S_m(0K) = 0 \qquad \text{... (ii)}$$

(Pure, perfectly-ordered crystal)

This convention establieshes a scale of absolute entropies at temperature above zero kelvins called ***third-law entropies.***

The temperature dependence of Entropy:

We have seen calculations for the entropy change for processes. However, it is also possible to calculate the absolute entropy. We can begin with the definities $\dfrac{dS_{rev}}{T}$. The heat transferred during a process at constant volume is $\dfrac{dS_{v/rev}}{T} = C_V dT$. Thus, the entropy change at constant volume is

$$dS = S(T) - S(0) = \int_0^T \frac{C_v(T)\,dT}{T}$$

We have kept the equation general by showing $C_V(T)$ as a function of temperature., This calculation of the entropy is valid only at contant V. At contant P we find an analoguous expression. Starting with the heat transferred, $dq_{p,rev} = C_P dT$

We have, $\Delta S = S(T) - S(0) \int_0^T \frac{C_P(T)\,dT}{T}$

The temperature dependence of the heat capacity:

The third law of thermodynamics shows that

$$C_P \to 0 \text{ as } T \to 0K$$

It is necessary to treat $C_P(T)$ as a function of temperature for this reason alone. The Einstsein and Debye theories of heat capacity can be used to determine the functional form of the heat capacity of at these low temperatures. The Debye law states that the heat capacity depends on T^3 near T = 0K.

At temperatures close to $\boxed{T = 0, C_{V,m} = aT^3}$

The constant a is an empirical constant. For practical calculation of the entropy experimental values can be used and the integrals are evaluated numerically.

Problem : Show that the entropy of any substance at very low temperature (0 < T < 20 K), where Debye's relation for heat capacities of crystals is valid, is one-third of the molar heat capacity.

Soln. Since we know that, at low temperature (0 < T < 20 K)

$$C_P = aT^3 \qquad \text{... (i)}$$

$$dS = \left(\frac{C_P}{T}\right) dT$$

$$\therefore \quad \int_0^T dS = \int_0^T (C_p / T)\,dT$$

Or, $$S_T - S_0 = \int_0^T \frac{aT^3}{T} dT = a\int_0^T T^2 dT = \frac{a}{3}T^3$$

Or, $$S_T = \frac{aT^3}{3}$$

From equation (i), we get

$$S_T = \frac{C_P}{3}$$

Absolute Entropy:

The absolute entropy can be calculated from 0 to any temperature T using the integral of the function, $\frac{C_p(T)}{T}$.

If there is a phase transition between 0 and temperature T we can also calculate the contribution to the entropy from the transition.

$$S(T) = \int_0^{T_{fus}} \frac{C_p(T)\,dT}{T} + \frac{\Delta H_{fus}}{T_{fus}} + \int_{T_{fus}}^{T_{vap}} \frac{C_p(T)\,dT}{T} + \frac{\Delta H_{vap}}{T_{vap}} + \int_{T_{vap}}^{T} \frac{C_p(T)\,dT}{T}$$

The heat capacity of each phase is different and the heat capacities are also a function of temperature.

Residual Entropy:

Residual entropy is the different in entropy between a non-equilibrium state and crystal state of a substance close to absolute zero.

There are certain solid which do not have perfect crystalline structure at 0°K like as H_2, D_2, CO, NO, N_2O and H_2O. So, they have certain amount of entropy even at absolute zero. This is called residual entropy.

According to third law of thermodynamics for perfect crystalline solid at zero Kelvin the entropy change in zero. But certain solid at zero kelvin the entropy does not found the zero. So, this is not follow this rule.

Residual Entropy $\propto$ probability of arrangement of one molecule of the atom.

So, for Boltzmann's rule,

$$\boxed{S = k \ln w}$$

where S is residual entropy, K boltzmann's constant and w is probability of arrangment of 1 mole of the atom.

CO, an imperted Crystal:

The molecule CO has a very small dipole moment and there is a finite chance that CO will crystalline as CO : CO : CO instead of CO : CO : CO. For each CO molecule there are two possible orientations of the molecule, therefore, there are two ways each CO can exist in the lattice. The number of ways per molecule is w = 2 for each CO. If we have N CO molecules there are w^N ways or 2^N ways that all of the CO can be distributed. Therefore, the entropy at zero Kelvin is

$$S = k \ln W = k \ln\left(w^N\right) = Nk \ln w = R \ln w = R \ln 2$$

Where, R = Nk

The entropy at zero Kelvin is known as residual entropy. There are number of substances that show similar statistical variations in orientation that lead to a residual entropy.

PROBLEMS

1. The molar entropy of crystalline CO at absolute zero is: **[GATE 2010]**

(a) Zero (b) –Rln2 (c) Rln2 (d) 2Rln2

Soln. For 1 mole of certain monoxide, $w = 2^N$

Since we know that, $S = k \ln w$

$$S = k \ln 2^N$$

$$S = Nk \ln 2$$

$$S = R \ln 2 \qquad (\because \ R = Nk)$$

Correct option is (c)

Remarks:

Translational entropy of the molecule

$$S_{tr} = \ell n\left(\frac{2\pi mkT}{h^2}\right)^{3/2} \frac{V e^{5/2}}{N_A}$$

Where, V= Volume of the system, N_A = Avogadro's number, m = Mass of the molecule
h = Planck's constant; k = Boltzmann's constant, T = absolute temperature (K)

Rotational entropy of the molecule

$$S_{rot} = Nk\ell n\left[\frac{\pi^{1/2}}{\sigma}\prod_{j=1}^{3}\left(\frac{8\pi^2 I_j kT}{h^2}\right)^{1/2}\right]$$

Where, I_j = Principal moments of inertia of the molecule,

σ = Symmetry number of the molecule.

h = Planck's constant, k = Boltzmann's constant,

T = absolute temperature (K)

Vibrational entropy of the molecule.

$$S_{vib} = \sum_{j=1}^{\alpha}\left\{\frac{hV_j \exp\left(-hV_j/2kT\right)}{kT\left[1-\exp\left(-hV_j/2kT\right)\right]} - \ell n\left[1-\exp\left(-hV_j/2kT\right)\right]\right\}$$

Where, n_j = Frequencies of normal vibrations in molecule,

k = Boltzmann's constant

T = Absolute temperature (K)

h = Planck's constant

PRACTICE SET

1. Standard entropy of crystalline carbon monoxide (in kJ/mol) at 0K is around
   (a) 0.03 (b) 2.50 (c) zero (d) 5.76

2. Suppose there are four ways the molecule CFClBrI can be oriented in a crystal lattice at zero Kelvin. What is the molar residual entropy?
   (a) 4R ln(2) (b) 2R ln(4) (c) R ln(2) (d) R ln(4)

3. Which phrase best summarizes residual entropy?
   (a) The entropy of imperfect crystals (b) The entropy of the lowest energy state
   (c) The entropy of rotation (d) The entropy of residues

4. If there is no residual entropy then at T = 0 K we can state that
   (a) $S > 0$ and $C_p > 0$ (b) $S = 0$ and $C_p > 0$ (c) $S > 0$ and $C_p = 0$ (d) $S = 0$ and $C_p = 0$

5. Consider the statement $C_P \to 0$ as $T \to 0$. Which consequence is valid.
   (a) It is harder to heat matter near absolute zero, that is it requires more energy per degree of temperature rise.
   (b) It is easier to heat matter near absolute zero, that is it requires less energy per degree of temperature rise.
   (c) It gets easier to reach absolute zero because it is easier cool matter at lower temperature
   (d) Both (b) and (c) are correct.

ANSWER KEY					
Questions	1	2	3	4	5
Option	(d)	(d)	(a)	(d)	(b)

Chapter 6

Partial Molar Quantity

Expression of Partial Molar Quantity

Thermodynamic relations derived earlier are applicable to the closed system but if we discuss a system where not only the work and heat but matter are being exchanged, we need partial molar quantity.

For example : Gibb's free energy of a system is a function not only of temperature and pressure, but also of the amount of each substance in the system, such that

$$G = f\left(T, P, n_1, n_2, n_3 \ldots . n_k\right)$$

where $n_1, n_2, \ldots\ldots\ldots n_k$ represent the amount of each of the k components in the system. For simplicity, let a system contain only two components. The total differential of G is

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2,n_3 \ldots\ldots n_k} + \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2,n_3,\ldots\ldots n_k} + \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2,n_3,\ldots\ldots n_k} + \left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_1,n_3,\ldots\ldots n_k}$$

In this equation $\left(\frac{\partial G}{\partial n_1}\right)$ and $\left(\frac{\partial G}{\partial n_2}\right)$ are known as partial molar free energy of component 1 and 2, respectively.

In general, the partial derivatives of a thermodynamic function (y) with respect to the amount of component (i) of a mixture, when temperature, pressure and other constituents are kept constant is known as partial molar quantity of i^{th} component and is represented as $Y_{i,pm}$ (or simply as Y_i). Thus

$$Y_{i,pm} = \left(\frac{\partial Y}{\partial n_i}\right)_{T,p,n_{j\neq i}}$$

The various partial molal quantity are:

(1) Partial molal internal energy $\bar{E}_i = \left(\frac{\partial E}{\partial n_i}\right)_{P,T,n_1,n_2\ldots\ldots}$

(2) Partial molal enthalpy energy $\bar{H}_i = \left(\frac{\partial H}{\partial n_i}\right)_{P,T,n_1,n_2\ldots.}$

(3) Partial molar Gibb's free $\bar{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_1,n_2\ldots\ldots}$ (chemical potential)

(4) Partial molal work function $\bar{A}_i = \left(\frac{\partial A}{\partial n_i}\right)_{P,T,n_1,n_2}$

(5) Partial molal volume $\bar{V}_i = \left(\frac{\partial V}{\partial n_i}\right)_{P,T,n_1,n_2\ldots.}$

The most useful partial molal quantity is partial molal free energy. It is known as chemical potential (μ_i). The name chemical potential is not given to the partial Gibb's free energies but also all partial thermodynamic potential in respect of their natural variables.
The various chemical potential are as:

(1) $\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_1,n_2.....}$ (2) $\left(\frac{\partial A}{\partial n_i}\right)_{V,T,n_1,n_2.....}$ (3) $\left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_1,n_2.....}$ (4) $\left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_1,n_2.....}$

Definition of partial Molar quantity:
The partial molar quantity may be defined in either of the following two ways:

(1) It is the change in Y when 1 mole of component *i* is added to a system which is so large that this addition has a negligible effect on the composition of the system.

(2) Let dY be the change in value of Y when an infinitestimal amount dn_i of component *i* is added to It is change in 'y' when 1 mole of component 'i' is added to the system of definite composition. By an infinitesimal amount dn_i we mean that its addition does not cause any appreciable change in the composition of the system. If we divide dY by dn_i, we get the partial molar quantity $\left(\frac{\partial Y}{\partial n_i}\right)$. Thus, the partial molar quantity of component *i* may be defined as the change in Y per mole of component i when an infinitesimal amount of this component is added to a system of definite composition.

Chemical Potential (μ) :
The most useful partial molar quantity is the partial molar free energy $G_{i,pm}$. It is so useful that it is given the name of chemical potential and a separate symbol μ_i to emphasis its generality.

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{\substack{T,p,n_j s \\ j\neq i}} \quad \text{... (1)}$$

Chemical potential is an intensive property because it is a molar quantity.
The thermodynamics properties likes E, H, S, A and G are extensive property. In case of open system, extensive property live G is a function not only of temperature and pressure but also the number of moles of various components present in the system

$$G = f\left(T, P, n_1, n_2, n_3, ...n_i\right)$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_j s} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_j s} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T,p,n_2.....n_i} dn_1 + ...+ \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_1,n_2.....} dn_i$$

The quantity $\left(\frac{\partial G}{\partial n_1}\right)_{T,p,n_2.....n_j}$ is the partial molar free energy and is represented by $\vec{G}_i$ or μ_i known as chemical potential of the component *i*.

$$\vec{G}_i = \mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_1,n_2}$$

Hence, chemical potential of a system substance may be defined as the change in free energy of the system when 1 mole of that substance is added at constant temperature and pressure.
Thus, equation for change in free energy of the systesm may be written as

$$\partial G = \left(\frac{\partial G}{\partial T}\right)_{P,n_j s} dT + \left(\frac{\partial G}{\partial p}\right)_{T,n_j s} dP + \mu_1 dn_1 + \mu_2 dn_2 + ... + \mu_i dn_i$$

Physical Significance:

(1) It represents the partial change in free energy with respect to its number of moles at constant temperature and pressure.

$$(\partial G)_{T,P} = \mu_1 dn_1 + \mu_2 dn_2 + ... + \mu_i dn_i$$

on integrating we get,

$$G_{T,p,n} = \mu_1 n_1 + \mu_2 n_2 + ... + \mu_j n_i$$

(2) It is an intensive property and may be regarded as the driving force that complex a system to attain an equilibrium

(3) At equilibrium the chemical potential of a substance has the same value through the system i.e. $\sum \mu_i dn_i = 0$

(4) For 1 mole of pure substance, the chemical potentials is identical to the free energy $\mu = G$

(5) It has great importance to drive Gibbs Duhem equation.

Expressions of dU, dH, dA and dG for multicomponent open system:

If a system contains a total of k components, then

$$G = f(T, P, n_1, n_2, ..., n_k)$$

Its differential is given by

$$\partial G = \left(\frac{\partial G}{\partial T}\right)_{P,n_j s} dT + \left(\frac{\partial G}{\partial p}\right)_{T,n_j s} + \sum_{i=1}^{k} \left(\frac{\partial G}{\partial n_i}\right)_{\substack{T,P,n_j s \\ j \neq i}} dn_i$$

Substituting equation (1) in the above equation, we get

$$\partial G = \left(\frac{\partial G}{\partial T}\right)_{P,n_j s} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_j s} dp + \sum_{i=1}^{k} \mu_i dn_i$$

$$dG = -SdT + VdP + \sum_{i=1}^{k} \mu_i dn_i \quad \ldots (2)$$

Now, since A = G – PV, therefore,

$$dA = dG - PdV - VdP$$

Substituting for dG from equation (2), we get

$$dA = \left(-SdT + VdP + \sum_{i=1}^{k} \mu_i dn_i\right) - PdV - VdP$$

$$= -SdT - PdV + \sum_{i=1}^{k} \mu_i dn_i \quad \ldots (3)$$

Similarly, for enthalpy

$$H = G + TS$$

$$dH = dG + TdS + SdT$$

$$= \left(-SdT + VdP + \sum_{i=1}^{k} \mu_i dn_i\right) + TdS + SdT$$

$$= TdS + VdP + \sum_{i=1}^{k} \mu_i dn_i \quad \ldots (4)$$

and for energy U = H – PV

$$dU = dH - PdV - VdP$$

$$= \left(TdS + VdP + \sum_{i=1}^{k} \mu_i dn_i\right) - PdV - VdP$$

$$= TdS - PdV + \sum_{i} \mu_i dn_i \quad \ldots (5)$$

If the amounts of all components are held constant, then equation ( ) to ( ) are reduced to

$$dG = -SdT + VdP \quad \text{... (6)}$$

$$dA = -SdT - PdP \quad \text{... (7)}$$

$$dH = TdS + VdP \quad \text{... (8)}$$

$$dU = TdS - PdV \quad \text{... (9)}$$

Equations (3) to (9) are applicable to closed systems.
From equation (2), it follows that

$$\mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{\substack{T,V,n_j s \\ j\neq i}} \quad \text{... (10)}$$

Similarly from equation (4) and (5), we have

$$\mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{\substack{S,P,n_j s \\ j\neq i}} \quad \text{... (11)}$$

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{\substack{S,V,n_j s \\ j\neq i}} \quad \text{... (12)}$$

Hence,
$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{\substack{T,P,n_j s \\ j\neq i}} = \left(\frac{\partial A}{\partial n_i}\right)_{\substack{T,V,n_j s \\ j\neq i}} = \left(\frac{\partial H}{\partial n_i}\right)_{\substack{S,P,n_j s \\ j\neq i}} = \left(\frac{\partial U}{\partial n_i}\right)_{\substack{S,V,n_j s \\ j\neq i}} \quad \text{... (13)}$$

From equation (13), it is obvious that the chemical potential plays a different role in each equation (1) to (4), even through it is the same quantity in all cases.

Variation of chemical potential with temperature and pressure:

$$dG = \left(\frac{dG}{dT}\right)_{P,n_j s} dT + \left(\frac{dG}{dP}\right)_{T,n_j s} dP + \mu_1 dn_1 + \mu_2 dn_2 + ... + \mu_i dn_i$$

$$(dG)_n = \left(\frac{dG}{dT}\right)_{P,n_j s} dT + \left(\frac{dG}{dP}\right)_{T,n_j s} dP$$

$$dsG = VdP - SdT$$

by equating the coefficient of dT and dP in the above two equations, we get

$$\left(\frac{dG}{dT}\right)_{P,n} = -S \text{ and } \left(\frac{dG}{dP}\right)_{T,n} = V$$

Which are applicable to a single-component system become

$$\left(\frac{d\mu_i}{\partial T}\right)_{P,n_j s} = -S_i \text{ and } \left(\frac{d\mu_i}{\partial P}\right)_{T,n_j s} = V_i$$

for a multicomponent open system. These equations may be proved as follows:

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n_j s} = \left\{\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial n_i}\right)_{\substack{T,P,n_j s \\ j\neq i}}\right\}_{P,n_j s} = \left\{\frac{\partial}{\partial n_i}\left(\frac{\partial G}{\partial T}\right)_{\substack{P,n_j s \\ j\neq i}}\right\}$$

[since the order of differential does not matter as G is a state function]

$$= \left\{ \frac{\partial}{\partial n_i}(-S) \right\}_{T,P,n_j s \atop j \neq i} = -S_i$$

Similarly, $$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,n_j s} = \left\{ \frac{\partial}{\partial P}\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{js} \atop j=i} \right\}_{T,n_j s} = \left\{ \frac{\partial}{\partial n_i}\left(\frac{\partial G}{\partial P}\right)_{T,n_j s} \right\}_{T,P,n_j s \atop j=i}$$

$$= \left\{ \frac{\partial}{\partial n_i}(V) \right\}_{T,P,n_j s \atop j=i} = V_i$$

$$\Rightarrow \quad \left(\frac{\partial \mu_i}{\partial P}\right)_{T,n_j s} = V_i \qquad \ldots (1)$$

Since, we know that PV = RT $\Rightarrow$ $V = \frac{RT}{P}$

From equation (1), $\left(\frac{\partial \mu_i}{\partial P}\right) = \frac{RT}{P}$

$$\Rightarrow \quad \int_{\mu_i^0}^{\mu_i} d\mu_i = RT \int_{P^0}^{P} \frac{dP}{P} \qquad \Rightarrow \left[\mu_i\right]_{\mu_i^0}^{\mu_i} = RT\left[\ell n P\right]_{P^0}^{P}$$

$$\Rightarrow \quad \mu_i - \mu_i^0 = RT\left[\ell n P - \ell n P^0\right] \Rightarrow \mu_i - \mu_i^0 = RT \ell n \frac{P}{P^0}$$

$$\therefore \quad \boxed{\mu_i = \mu_i^0 + RT \ell n \frac{P}{P^0}}$$

where, μ_i^0 = standard chemical potential.

μ_i is the standard chemical potential when the pressure of the gas is 1° bar. It may be noted that μ_i depend on both *T* and P but μ_i^0 depend only on T.

Gibb's - Duhem equation:

Since, we know that,

$$G_{T,P,n} = \mu_1 n_1 + \mu_2 n_2 + ... + \mu_i n_i$$

On differentially,

$$dG = \mu_1 dn_1 + n_1 d\mu_1 + \mu_2 d\mu_2 + ... + \mu_i dn_i + n_i d\mu_i$$

$$dG = \left[\mu_1 dn_1 + \mu_2 dn_2 + ... + \mu_i dn_i\right] + \left(n_1 d\mu_1 + n_2 d\mu_2 + ... + n_i d\mu_i\right)$$

But we know that,

$$\left(dG\right)_{T,P} = \left(\mu_1 dn_1 + \mu_2 dn_2 + ... + \mu_i dn_i\right)$$

Therefore, $$\left(n_1 d\mu_1 + n_2 d\mu_2 + ... + n_i d\mu_i\right) = 0$$

Or, $$\boxed{\sum n_i d\mu_i = 0}$$

This reaction is general form of Gibbs Duhem equation. For a binary solution.

$$n_1 d\mu_1 + n_2 d\mu_2 = 0$$

$$\boxed{d\mu_1 = -\frac{n_2}{n_1} d\mu_2}$$

Chemical Potential of a gas in mixture of ideal gases:

The expression for the chemical potential of an ideal gas in a mixture of ideal gases can be obtained by replacing P in equation ($\mu = \mu^0 + RT \ln\left(\frac{P}{P^0}\right)$) by the partial pressure of the gas in the gaseous mixture. Thus.

$$\mu_{i(mix)} = \mu_i^0 + RT \ln\left(\frac{P_i}{P^0}\right)$$

where, $P^0 = 1$ bar. Since $P_i = x_i P$, therefore,

$$\mu_{i(mix)} = \mu_i^0 + RT \ln\left(\frac{P}{P^0}\right) + RT \ln x_i$$

$$= \mu_i^* + RT \ln x_i \qquad \ldots (1)$$

where, μ_i^* represents the chemical potential of the pure ideal gas at temperature T and pressure P and is given as

$$\mu_i^* = \mu_i^0 + RT \ln\left(\frac{P}{P^0}\right)$$

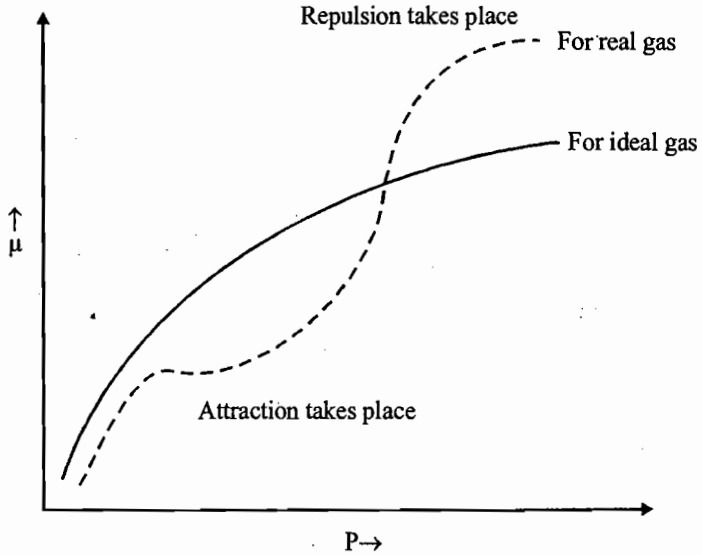
Since, $x_i < 1$, the term $RT\ell nx_i$ in equation (1) has a negative value. It, therefore, follows that

$$\mu_{i(mix)} < \mu_i^*$$

that is, the chemical potential of an ideal gas in a mixture of ideal gases with a total pressure P is less than the corresponding value for the pure ideal gas at the smae total pressure P.

Graph between chemical potential $\mu_{(T,P)}$ and pressure (P) :

$$\mu = \mu_0 + RT \ln P$$



(1) In moderate range of pressure attraction between the molecule is considerable in real gas. Pressure for real gas in terms of chemical potential is less than the pressure of ideal gas.

(2) For high pressure region the molecule for real gas start repalled to each other so P for real gas in terms chemical potential becomes higher than the ideal gas.

Concept of Fugacity :

Making use of the free energy function, **G, Lewis** introduced the concept of **fugacity** for representing the actual behaviour of real gases which is distinctly different from the behaviour of ideal gases.

Variation of free energy with pressure at constant temperature is given by

$$\left(\frac{\partial G}{\partial P}\right)_T = V \qquad \ldots (1)$$

This equation is applicable to all gases whether ideal or non-ideal.

If one mole of a gas is under consideration, then V refers to molar volume. For an ideal gas, the above equation may be written as

$$(dG)_T = RT\frac{dP}{P} \qquad \ldots (2)$$

and for n moles as,

$$(dG)_T = nRT\frac{dP}{P} = nRT(\ln P) \qquad \ldots (3)$$

Integration of equation, (3) yields

$$G = G^* + nRT\ln P \qquad \ldots (4)$$

where G^*, the integration constant, is the free energy of n moles of the ideal gas at temperature T when the pressure P is unity.

Equation (4) evidently, gives the free energy of an ideal gas at temperature T and pressure P.

Integration of equation (3) between pressures P_1 and P_2, at constant temperature T, yields,

$$\Delta G = \int_{P_1}^{P_2} nRT\frac{dP}{P} = nRT\ln\frac{P_2}{P_1} \qquad \ldots (5)$$

The corresponding equation for 1 mole of the gas would be

$$\Delta G = RT\ln\frac{P_2}{P_1} \qquad \ldots (6)$$

Equation (4) and (6) are not valid for real gases since V is not exactly equal to $\frac{RT}{P}$

In order to make these simple equations applicable to real gases, Lewis introduced a new function f, called ***fugacity function***. It takes the place of P in equation (3) which, for real gases, may be expressed as

$$(dG)_T = nRTd(\ln f) \qquad \ldots (7)$$

and equation (4) may be represented as

$$G = G^* + nRT\ln f \qquad \ldots (8)$$

where, G^* is the free energy of n moles of a real gas when its fugacity happens to be 1.

Thus, fugacity is a sort of **'frictious pressure'** which is used in order to retain for real gases simple forms of equations which are applicable to ideal gases only.

Equation (8), evidently, gives the ***free energy of a real gas*** at temperature T and pressure P at which its fugacity can be taken as f.

Equation (7), on integration between fugacities f_1 and f_2, at constant temperature T, yields

$$\Delta G = G_2 - G_1 = nRT\ln\left(\frac{f_2}{f_1}\right) \qquad \ldots (9)$$

The corresponding equation for 1 mole of the gas would be

$$\Delta G = G_2 - G_1 = RT\ln\left(\frac{f_2}{f_1}\right) \qquad \ldots (10)$$

Or,

$$\boxed{\Delta\mu = \mu_2 - \mu_1 = RT\ln\frac{f_2}{f_1}} \qquad \ldots (11)$$

The Fugacity Coefficient:

In general, the fugacity of a real gas is related to its pressure by an equation

$$\frac{f}{p} = \gamma$$

where γ is known as the fugacity coefficient and is a measure of deviations of a real gas from the ideal behaviour. Since all gases approach ideality in the limit of zero pressure, it is obvious that

$$\lim_{p\to 0} \frac{f}{p} = \lim_{p\to 0} \gamma = 1 \qquad \ldots (13)$$

The fugacity is expected in the same units as pressure and thus the fugacity coefficient is a pure number.

Evaluation of Fugacity:

Equation $dG = VdP$ is applicable for all substances. Expressing it in terms of molar quantities and then using equation (10) and (11) separately, we get

$$\int_{P_1}^{P_2} V_{m,ideal}\, dP = \mu_{P_2,ideal} - \mu_{P_1,ideal} = RT \ln \frac{P_2}{P_1} \quad \text{(where, } V_m \text{ is molar value)}$$

$$\int_{P_1}^{P_2} V_{m,real}\, dP = \mu_{P_2,real} - \mu_{P_1,real} = RT \ln \frac{f_2}{f_1}$$

Taking the difference, we have

$$\int_{P_1}^{P_2} \left(V_{m,real} - V_{m,ideal}\right) dP = RT \ln \frac{f_2}{f_1} - RT \ln \frac{P_2}{P_1}$$

Or,
$$RT \ln \left(\frac{f_2}{f_1}\right)\left(\frac{P_1}{P_2}\right) = \int_{P_1}^{P_2} \left(V_{m,real} - V_{m,ideal}\right) dP$$

Let P_1 be allowed to approach zero value, then from equation (13), we get

$$\lim_{P_1\to 0} \frac{f_1}{P_1} = 1$$

With this, the previous equation becomes

$$RT \ln \left(\frac{f_2}{P_2}\right) = \int_0^{P_2} \left(V_{m,real} - V_{m,ideal}\right) dP$$

Now for a real gas,

$$V_{m,real} = Z\frac{RT}{P} = Z\, V_{m,ideal}$$

where Z is the ***compression factor***. Introducing this in the previous expression, we get

$$\boxed{\ln \left(\frac{f_2}{P_2}\right) = \int_0^{P_2} \frac{Z-1}{P} dP}$$

Fugacity at low pressure :

The ratio $\frac{f}{P}$, where P is the actual pressure, approaches unity when P approaches zero since in that case a real gas approximate to ideal behaviour. The fugacity function, therefore, may be defined as

$$\lim_{P\to 0}\frac{f}{P}=1 \qquad \ldots (12)$$

Evidently, at low pressures, fugacity is equal to pressure. The two terms differ materially only at high pressures.

Fugacity for vander Waals gas:

Since, we know that

$$\left(P+\frac{a}{V_m^2}\right)\left(V_m\right)=RT$$

Or, $$Z=\frac{PV_m}{RT}=1-\frac{a}{V_mRT}$$

i.e. $$Z<1$$

Hence, f less than P is due to the constant 'a'. At high pressure, the vander Waals equation takes the form

$$\left(P\right)\left(V_m-b\right)=RT$$

Or, $$Z=\frac{PV_m}{RT}=1+b\frac{P}{RT}$$

i.e. $$Z>1$$

Hence, f greater than P is due to constant b. Thus, the neglect of the term b in vander Waals equationj makes f less than P and that of a makes it greater than P.

PROBLEMS

1. At any temperature T, the fugacity coefficient (γ) is given by **[GATE 2010]**

$$\ln\gamma=\int_0^P\frac{Z-1}{P'}dP'$$

where Z is the compressiblity factor. The fugacity coefficient of a real gas governed by equations of state, P(V–b) = RT with 'b' a constant is given by

(a) $\frac{RT}{bP}$ (b) $e^{\frac{RT}{bP}}$ (c) $\frac{bP}{RT}$ (d) $e^{\frac{bP}{RT}}$

Soln. $$\ln\gamma=\int_0^P\frac{Z-1}{P}dP \qquad \ldots (1)$$

Since, we know that the compressibility factor, $Z=\frac{PV}{RT}$

$P\left(V-b\right)=RT$; $PV-Pb=RT$; $PV=RT+Pb$

Both side divided by RT, $\frac{PV}{RT}=\frac{RT}{RT}+\frac{Pb}{RT}$

$Z=1+\frac{Pb}{RT}$ Put this value in equation (1)

$$\ln\gamma=\int_0^P\frac{1+\frac{Pb}{RT}-1}{P}dP \Rightarrow \ln\gamma=\int_0^P\frac{\frac{Pb}{RT}}{P}dP=\frac{Pb}{RT}$$

$\Rightarrow \quad \gamma=e^{\frac{bP}{RT}}$

Correct option is (d)

2. What is the free energy change accompanying the compression of 1 mole of a gas at 57°C from 25 to 200 atm. The fugacities of the gas at 57°C may be taken as 23 and 91 atm respectively at pressure of 25 and 200 atm.
(a) 3730.0 J (b) 3630.0 J (c) 3530.1 J (d) 3330.2 J

Soln. We know that,

$$\Delta G = nRT \ln \frac{P_2}{P_1} = 1\ mol\left(8.314\ JK^{-1}\ mol^{-1}\right)(330K) \ln \frac{200\ atm}{25\ atm} = 5702.8J$$

Now,

$$\Delta G = nRT \ln \frac{f_2}{f_1} = 1\ mol\left(8.314\ JK^{-1}\ mol^{-1}\right)(330K) \ln \frac{91\ atm}{23\ atm} = 3730.0J$$

Correct option is (a)

3. Show that,

$$\left(\frac{\partial(\Delta\mu_i / T)}{\partial T}\right)_{p,n_j s} = -\frac{\Delta H_i}{T^2}$$

Soln. We prove the above equation as follows:

$$\left(\frac{\partial(\Delta\mu_i / T)}{\partial T}\right)_{p,n_j s} = -\frac{1}{T^2}\Delta\mu_i + \frac{1}{T}\left(\frac{\partial}{\partial T}\Delta\mu_i\right)_{P,n_j s} = -\frac{1}{T^2}\Delta\mu_2 + \frac{1}{T}\left(-\Delta S_{i_{\mu_f}}\right)$$

$$= -\frac{1}{T^2}\left(\Delta H_i - T\Delta S_i\right) + \frac{1}{T}\left(-\Delta S_i\right) = -\frac{\Delta H_i}{T^2}$$

4. Show that the change

2 mol of an ideal gas (2 bar, 273K) $\rightarrow$ 2 mol of gas (1 bar, 273 K)

carried out irreversibly against an external pressure of 1 bar is spontaneous.

Soln. ΔG for the process can be calculated using the expression

$$\Delta G = nRT \ln \frac{P_2}{P_1}$$

Substituting the given values, we get

$$\Delta G = (2.0\ mol)\left(8.314\ JK^{-1}mol^{-1}\right)(273K)(2.303)\log\left(\frac{1\ bar}{2\ bar}\right)$$

$$= -3.147.06\ J.$$

Since, there occurs a decrease in the value of ΔG, it must therefore, be a spontaneous change.

5. Show that if equation of state for a gas is

$$P(V_m - b) = RT$$

where b is a constant, the fugacity of the gas is given by

$$\ln \frac{f}{p} = \frac{bp}{RT}$$

Also show that if $\frac{bP}{RT}$ is small (applicable at low pressure) this equation reduces to $\frac{f}{P} = \frac{P}{P_{ideal}}$

where P_{ideal} is the pressure the gas would exert if it were to be ideal but with the same molar volume as the real gas at pressure P.

Soln. We know that, $P(V_m - b) = RT$

Or, $Z = \frac{PV_m}{RT} = 1 + \frac{Pb}{RT}$

Substituting this in the relation,

$$\ln \frac{f}{P} = \int_0^P \frac{Z-1}{P} dP$$

and integrating the resultant expression, we get

$$\ln \frac{f}{P} = \frac{bP}{RT} \text{ or } \ln \frac{f}{P} = \exp\left(\frac{bP}{RT}\right)$$

If $\frac{bP}{RT}$ is small, we may write

$$\frac{f}{P} = 1 + \frac{bP}{RT} = \frac{RT + bP}{RT}$$

From the given equation of state, we have

$$RT + bP = PV_m$$

Hence, $\frac{f}{P} = P\left(\frac{V_m}{RT}\right) = \frac{P}{P_{ideal}}$

Or, $P^2 = f\, P_{ideal}$

that is, pressure of the gas is the geometric mean of the ideal pressure and fugacity.

6. For the reaction,

$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightarrow NH_3(g), \Delta G^0_{298K} = -16.45\ kJ\ mol^{-1}$ and $\Delta H^0_{298K} = -46.11\ kJ\ mol^{-1}$.

What is the value of ΔG^0_{500K} if ΔH^0 is considered independent of temperature.

(a) 5.89 kJ mol^{-1} (b) –5.89 kJ mol^{-1} (c) 3.66 kJ mol^{-1} (d) –3.66 kJ mol^{-1}

Soln. We know that,

$$\Delta G^0_T = \Delta H^0 + \frac{T}{T_0}\left(\Delta G^0_{T_0} - \Delta H^0\right)$$

We get,

$$\Delta G^0_T = -46.11\ kJ\ mol^{-1} + \left(\frac{500K}{298K}\right)\left(-16.45\ kJ\ mol^{-1} + 46.11\ kJ\ mol^{-1}\right)$$

$$= 3.66\ kJ\ mol^{-1}$$

Correct option is (c)

7. The fugacity coefficient ϕ is given by $\ln \phi = \int_0^P \left(\frac{z-1}{p}\right) dp$ where z is the compressibility factor, and p the pressure. The fugacity of a gas governed by the gas law $p(V_m - b) = RT$ is **[GATE 2004]**

(a) $p \ln(V_m / RT)$ (b) $pe^{b/RT}$ (c) $pe^{-bp/RT}$ (d) $pe^{bp/RT}$

Soln. $\ln \phi = \int_0^P \frac{Z-1}{P} dP$ ... (1)

Since, we know that the compressibility factor, $Z = \frac{PV_m}{RT}$

$P(V_m - b) = RT$

$PV_m - Pb = RT$

$PV_m = RT + Pb$

Both side divided by RT

$\frac{PV_m}{RT} = \frac{RT}{RT} + \frac{Pb}{RT}$

$Z = 1 + \frac{Pb}{RT}$ Put this value in equation (1)

$$\ln\phi = \int_0^P \frac{1 + \frac{Pb}{RT} - 1}{P} dP \Rightarrow \ln\phi = \int_0^P \frac{\frac{Pb}{RT}}{P} dP = \frac{Pb}{RT}$$

$$\Rightarrow \quad \phi = e^{\frac{bP}{RT}} \Rightarrow \phi = p\, e^{\frac{bP}{RT}}$$

Correct option is (d)

PRACTICE SET

1. The internal pressure $(\partial U/\partial V)_T$ of a real gas is related to the compressibility factor $Z = p\bar{V}/RT$ by $[\bar{V}$ is the molar volume$]$ **[NET Dec. 2012]**

(a) $(\partial U/\partial V)_T = RT(\partial Z/\partial V)_T$ (b) $(\partial U/\partial V)_T = RT/(\bar{V}\,Z)$

(c) $(\partial U/\partial V)_T = (RT^2/\bar{V})(\partial Z/\partial V)_V$ (d) $(\partial U/\partial V)_T = (\bar{V}/RT^2)(\partial Z/\partial T)_V$

2. The fugacity of a gas depends on pressure and the compressibility factor $Z(= p\bar{V}/RT)$ through the relation $(\bar{V}$ is the molar volume$)$.

For most gases at temperature T and up to moderate pressure, this equation shows that **[NET Dec. 2012]**

(a) $f < p$, if $T \to 0$ (b) $f < p$, if $T \to \infty$

(c) $f > p$, if $T \to 0$ (d) $f = p$, if $T \to 0$

3. The chemical potential (μ_i) of the i^{th} component is defined as **[NET Dec. 2013]**

(a) $\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{T,P}$ (b) $\mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{T,P}$ (c) $\mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{T,P}$ (d) $\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P}$

4. Given the following two relations, $x_1 d\mu_1 + x_2 d\mu_2 = 0$ (A) **[NET Dec. 2014]**

and $x_1 d\bar{V}_1 + x_2 d\bar{V}_2 = 0$, (B)

for a binary liquid mixture at constant temperature and pressure, the true statement is that,

(a) Both the relations are correct
(b) Relation A is correct, but B is not
(c) Relation B is correct, but A is not
(d) Both the relations are incorrect, except for very dilute solutions.

5. For a vander Waals gas

$$Z = 1 + \left[b - \left(\frac{a}{RT} \right) \right] \frac{P}{RT}$$

What is the fugacity at 100 bar and 298K. [Given : $a = 0.2476\ dm^6\ bar\ mol^{-2}$ and $b = 0.02661\ dm^3\ mol^{-1}$]
(a) 106.9 bar (b) 101.9 bar (c) 110.9 bar (d) 120.9 bar

6. What is the free energy change accompanyingthe compression of 1 mole of a gas at 25°C from 20 to 200 atm. The fugacities of the gas be taken as 18 and 120 atm atm, respectively at pressure of 18 and 200 atm.
(a) 4700 J (b) 4000 J (c) 4100 J (d) 3900 J

7. What is the fugacity of $H_2(g)$ at 100°C and 300 atm, assuming that it is a vander Waals gas, with $a = 0.244$ dm^6 atm mol^{-2}, $b = 0.0266$ dm^3 mol^{-1} and $V_m = 0.119$ dm^3 mol^{-1}.
(a) 485.5 atm (b) 386.6 atm (c) 286.6 atm (d) 586.6 atm

8. The expression which represents the chemical potential of the i^{th} species(μ_i) in a mixture $(i \neq j)$ is:

(a) $(\partial E / \partial n_i)_{s,v,nj}$ (b) $(\partial H / \partial n_i)_{s,v,nj}$ (c) $(\partial A / \partial n_i)_{s,v,nj}$ (d) $(\partial G / \partial n_i)_{s,v,nj}$ **[GATE 2007]**

ANSWER KEY					
Questions	1	2	3	4	5
Option	(c)	(a)	(d)	(a)	(a)
Questions	6	7	8		
Option	(a)	(b)	(a)		

Chapter 7

Thermochemistry

Introduction:

The chemistry dealing with heat changes in chemical reactions is known as thermochemistry.

Heat of formation:

The enthalpy change associated with the formation of 1 mole of compound from its element under standard condition.

e.g. $C + 2H_2 \longrightarrow CH_4$ $\Delta H_f = -18.50$ Kcal

$C + O_2 \longrightarrow CO_2$ $\Delta H_f = -96.96$ Kcal

Heat of combustion:

The enthalpy change associated with the complete combustion of 1 mole of substance.

e.g. $H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(g)}$ $\Delta H = -68.40$ Kcal

$S_{(g)} + O_{2(g)} \longrightarrow SO_{2(g)}$ $\Delta H = -71$ Kcal

Measuring the enthalpy of Combustion (Bomb Calorimeter) :

The calorimeter used for determining enthalpies of combustion, known as the bomb calorimeter, is shown in figure below (1) and (2).

The inner vessel or the 'bomb' (figure-2) and its cover are made of strong steel coated inside with gold or platinum or some other non-oxidisable material. The cover can be fitted tightly to the vessel by means of a metal lid screwed down on a lead washer. A weighed amount of the substance is taken in a platinum cup C which is supported on a rod R.

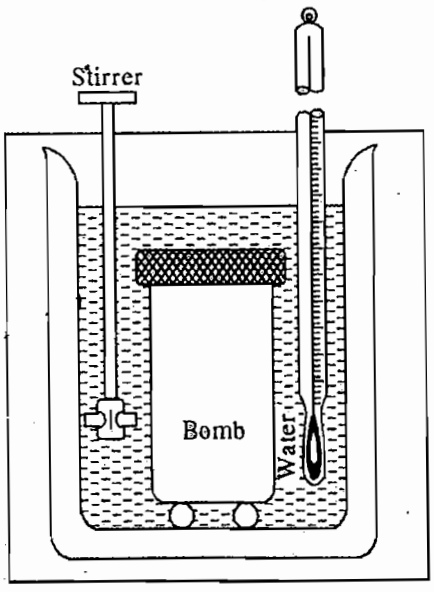


Figure-(1): Bomb calorimeter

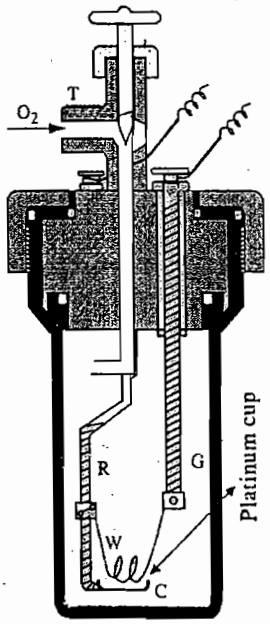


Figure-(2): The Bomb

A thin platinum wire W is connected between the rods R and G, as shown. This serves to initiate the combustion when heated electrically. The bomb is tightly closed and oxygen introduced through the inlet tube T until a pressure of about 20–25 atmospheres is attained. The bomb is then lowered in water placed in a double jacketed and polished metallic calorimeter so as to minimise error due to radiaton. A mechanical stirrer is provided as shown (figure (1)). When the temperature of the water has become steady, the substance is ignited by passing electric current through the platinum wire W. The rise of temperature of the water in the calorimeter is noted after every minute by means of a Beckmann thermometer graduated to read up to a hundredth of a degree. The final temperature when corrected for the radiation error in the usual way, minus the initial temperature, gives the rise of temperature.

The heat capacity of the calorimeter system is obtained by burning a known weight of a substance of known enthalpy of combustion. For this purpose, usually benzoic acid of high grade purity is taken. Its enthalpy of combustion which has been very carefully measured is taken as $-3226.7\ kJ\ mol^{-1}$.

Suppose the thermal capacity of the calorimeter system including water is z and θ is the rise in temperature produced by burning a quantity 'm' of the given substance of molar mass M. Then, evidently, the enthalpy of combustion of the substance is given by $\boxed{q_v = z \times \theta \times M/m}$.

Heat of neutralisation:

The enthalpy change associated with complete neutralisation of 1 equivalent of acid reacts with 1 equilivalent of base.

$$\Delta H_{(neutralisation)} = \Delta H_{(ionisation)} + \Delta H\left(H^+ + OH^-\right)$$

$\Rightarrow$ For strong acid-base pair $\Delta H = -13.7$ Kcal

$\Rightarrow$ For weak acid - base pair $\Delta H = -11.4$ Kcal

Heat of solution:

It is defined as the enthalpy changed when 1 mole of solute is dissolved completely in excess of solvent.

Heat of hydration:

Enthalpy change associated with the formation of 1 mole of a specified hydrate from 1 mole of an anhydrous substance on combustion with the required number of moles of water.

Hess's law of constant heat summation:

At constant pressure the total enthalpy change (ΔH) accompanying a chemical reaction is the same whether the reaction takes place in one or more steps.

e.g. for a reaction

$$A \longrightarrow D \qquad \Delta H = q$$

& for $A \xrightarrow[q_1]{} B \xrightarrow[q_2]{} C \xrightarrow[q_3]{} D$

Thus, according to this law

$$\boxed{q = q_1 + q_2 + q_3}$$

Bond energy:

It is defined as the average amount of energy required to break 1 mole of such bonds present in different compounds, the original molecules and the dissociated products being in the gaseous state. Bond energy is endothermic process.

The energy of formation a bond is numerically equal to its corresponding bond energy but with a negative sign(i.e. exothermic process).

Relation between enthalpy of reaction at constant volume and at constant pressure.

$\because$ $\Delta H = \Delta U + P\Delta V$ ... (1)

But we know

$$\Delta H = q_P$$

and $\Delta U = q_V$

Therefore, equation (1) becomes

$$\boxed{q_P = q_V + P\Delta V} \quad \ldots (2)$$

for 'n' moles of an ideal gas

$$PV = nRT$$

Let n_1 and n_2 are the number of moles of gaseous reactant and gaseous products respectively.

$$\therefore \quad P\Delta V = \Delta n_g RT$$

Δn_g =[number of mole of gaseous products]–[number of moles of gaseous reactant]

$$\therefore \quad \boxed{q_P = q_V + \Delta n_g RT} \quad \ldots (3)$$

Adiabatic flame temperature:

The temperature which the system attains if the changes in the system are carried out under adiabatic condition. It takes at either constant P or at constant volume for exothermic reaction.

At constant pressure:

For exothermic reaction under adiabatic condition, heat evolved would not be escape and hence increases temperature of system.

The increase in temperature can be takes in two steps.

(1) Reactant $(T_0, P) \rightarrow$ product (T_0, P) $\quad \Delta H_{T_0}$

(2) Product $(T_0, P) \rightarrow$ product (T_f, P) $\quad \Delta H_2$

The heat evolved in 2nd step is given as $\Delta H_2 = \int_{T_0}^{T_f} C_{P(product)} dT$

For overall reaction, $\text{Reactant}(T_0, P) \longrightarrow \text{Product}(T_f, P)$

$\therefore$ Net heat change

$$\Delta H = \Delta H_{T_0} + \Delta H_2$$

Since adiabatic process are isoenthalpic

$$\therefore \quad \Delta H = 0 \Rightarrow 0 = \Delta H_{T_0} + \Delta H_2$$

$$\therefore \quad \Delta H_2 = -\Delta H_{T_0}$$

$$\therefore \quad -\Delta H_{T_0} = \int_{T_0}^{T_f} C_{P(product)} . dT \Rightarrow -\Delta_r H_{T_0} = C_{P(product)} (T_f - T_0)$$

$$\boxed{T_f = -\frac{\Delta_r H_{T_0}}{C_{P(product)}} + T_0}$$

Note: If the compound is burnt in air number of mole of nitrogen also changes to final temperature and hence included in the $C_{P(product)}$

1 mole of O_2 = 4 mole of N_2 associated.

At constant volume:

If reaction takes place closed vessel under constant volume condition

$$\boxed{T_f = -\frac{\Delta_r U_{T_0}}{C_{V(product)}} + T_0}$$

SOLVED PROBLEMS

1. 0.50 g of benzoic acid was subjected to combustion in a bomb calorimeter when the temperature of the calorimeter system (including water) was found to to rise by 0.55°C. What is the enthalpy of combustion of benzoic acid at constant volume.

(a) 3200 kJ mol^{-1} (b) –3200 kJ mol^{-1} (c) 1600 kJ mol^{-1} (d) –1600 kJ mol^{-1}

Soln. Enthalpy of combustion at constant volume

$$q_v = z \times \theta \times M/m$$

$$= 23.85\ kJ\ mol^{-1} \times 0.55K \times 122\ g\ mol^{-1} / 0.50\ g = 3200.7\ kJ\ mol^{-1} = -3200.7\ kJ\ mol^{-1}$$

[Note : The enthalpy of combustion has always a negative sign]

Correct option is (b)

2. In a bomb calorimeter, the combustion of 0.5 g of compound A (molar mass = 50 g mol^{-1}) increased the temperature by 4K. If the heat capacity of the calorimeter along with that of the material is 2.5 kJ K^{-1}, the molar internal energy of combustion, in kJ, is **[NET June 2014]**

(a) 1000 (b) –1000 (c) 20 (d) –20

Soln. Molar internal energy of combution $= z \times \theta \times \frac{M}{m} = \frac{50 \times 4 \times 2.5}{0.5} = \frac{50 \times 10}{0.5} = \frac{50 \times 10 \times 10}{0.5} = \frac{5000}{5} = 1000\ kJ =$ – 1000 kJ

Note : Energy of combution has always a negative sign.

Correct answer is (b)

3. What is the relationship between q_P and q_V Haber synthesis of ammonia assuming that the gaseous reactants and products are ideal.

(a) $q_P = q_V - 2RT$ (b) $q_P = q_V + 2RT$ (c) $q_P = q_V - RT$ (d) $q_P = q_V + RT$

Soln. $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$, $\Delta n_g = 2 - (2+3) = -2$

$\therefore \quad q_P = q_V + \Delta n_g RT \Rightarrow q_P = q_V - 2RT$

Correct option is (a)

4. One mole of naphthalene was burnt in oxygen gas at constant volume to give carbon dioxide gas and liquid waer at 25°C. Heat evolved was found to be 5138.8 kJ. The enthalpy of reaction at constant pressure is [Given : R = 8.314 J/K-mol]

(a) 5143.8 kJ (b) –5143.8 kJ (c) 21430.01 kJ (d) –2143.01 kJ

Soln. $C_{10}H_{8(s)} + 12O_{2(g)} \rightarrow 10CO_{2(g)} + 4H_2O_{(\ell)}$

$\therefore \quad \Delta n_g = 10 - 12 = -2$

$\therefore \quad q_p = q_V + \Delta n_g RT = 5138.8 - 2 \times 8.314 \times 10^{-3}\ kJ / mole \times 298$

$\boxed{q_P = -5143.8\ kJ}$

Correct option is (b)

5. The enthalpy of combustion of glucose $C_6H_{12}O_{6(s)}$ is –2816 kJ/mol at 25°C. Calculate $\Delta H_f^0(C_6H_{12}O_6)$ values for CO_2, $O_{2(g)}$ & $H_2O_{(\ell)}$ are –393.5 and 285.9 kJ.mol^{-1}, respectively.

(a) 1360.5 kJ/mole (b) –1360.5 kJ/mole (c) –1260.4 kJ/mol (d) 1260.4 kJ/mol

Soln. $C_6H_{12}O_{(s)} + 6O_{2(g)} \longrightarrow 6CO_{2(g)} + 6H_2O_{(\ell)}$ $\Delta H^0 = -2816$ kJ

Since, $\Delta H = \sum \Delta H^0_{f_{(products)}} - \sum \Delta H^0_{f(reactant)}$

$\therefore$ $-2816 = 6\times(-393.5\text{ kJ}) + 6(-285.9\text{ kJ}) - \Delta H^0_f(C_6H_{12}O_6) - 6\Delta H^0_f(O_2)$

But $\Delta H^0_f(O_2) = 0$; $\Delta H^0_f(C_6H_{12}O_6) = -1260.4$ kJ/mole

Correct option is (c)

6. The heats of combustion of NH_3 and H_2 are 9.06 and 68.9 kcal respectively. The heat of formation of ammonia is

(a) 94.29 kcal (b) –94.29 kcal (c) 91.30 kcal (d) –91.20 kcal

Soln. We have to find,

(1) $\frac{1}{2}N_2 + \frac{3}{2}H_2 \longrightarrow NH_3$ $\Delta H^0_f = ?$

(2) $NH_3 + \frac{3}{4}O_2 \longrightarrow \frac{1}{2}N_2 + \frac{3}{2}H_2O$ $\Delta H = -9.06$ kcal

(3) $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$ $\Delta H = -68.9$ kcal

multiplying equation (3) by $\frac{3}{2}$ and then substracting equation (2) from equation (3)

$\frac{3}{2}H_2 + \frac{3}{4}O_2 - NH_3 - \frac{3}{4}O_2 \longrightarrow \frac{3}{2}H_2O - \frac{1}{2}N_2 - \frac{3}{2}H_2O$

$\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightarrow NH_3$ $\Delta H = \frac{3}{2}\times(-68.9) - (-9.06) = -94.29$ kcal

Correct option is (b)

7. The molar heats of combustion of $C_2H_{2(g)}$, $C_{(graphite)}$ and $H_{2(g)}$ are 31.62 kcal, 94.05 kcal and 68.32 kcal respectively. The standard heat of formation of $C_2H_{2(g)}$ is

(a) 54.20 kcal (b) 64.20 kcal (c) 74.20 kcal (d) 84.20 kcal

Soln. Given,

(i) $C + O_2 \rightarrow CO_2$ $\Delta H = -94.05$ kcal

(ii) $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ $\Delta H = -68.32$ kcal

(iii) $C_2H_2 + \frac{5}{2}O_2 \rightarrow 2CO_2 + H_2O$ $\Delta H = -310.62$ kcal

We have to find,

(iv) $2C + H_2 \rightarrow C_2H_2$ $\Delta H = ?$

$[2\times\text{equation (i)}] + \text{equation (ii)} - \text{equation (iii)}$

$$2C + 2O_2 + H_2 + \frac{1}{2}O_2 - C_2H_2 - \frac{5}{2}O_2 \rightarrow 2CO_2 + H_2O - 2CO_2 - H_2O$$

$\therefore$ $2C + H_2 \rightarrow C_2H_2$; $\Delta H = 2\times(-94.05) + (-68.32) - (-310.62) = 54.20$ kcal

Correct option is (a)

7. What is the heat of formation of benzene from the following data, assuming no resonance bond energies.

C – C = 83 kcal ; C = C = 140 kcal

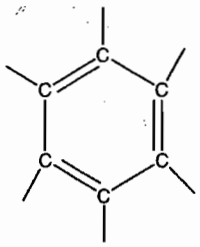
Heat of atomisation of C = 170.9 kcal

Heat of atomisation of H = 52.1 kcal

(a) 75 kcal (b) 85 kcal (c) 100 kcal (d) 120 kcal

Soln. We have to find ΔH of following reaction

$$6C_{(s)} + 3H_{2(g)} \rightarrow C_6H_{6(g)}$$



$\Delta H = ?$

For reactant:

Heat of atomisation of moles of C = 6×170.9 kcal

Heat of atomisation of moles of H = 6×52.1 kcal

For products:

Heat of formation of 6 moles of C–H bonds = –6×99 kcal

Heat of formation of 3 moles of C–C bonds = –3×83 kcal

Heat of formation of 3 moles of C=C bonds = –3×140 kcal

On adding, we get heat of formation of C_6H_6 i.e.

$\Delta H = 6\times170.9 + 6\times52.1 - 6\times99 - 3\times83 - 3\times140 = 75.0$ kcal

Correct option is (a)

8. What is the resonance energy in CH_3COOH from the following data if the observed heat of formation of CH_3COOH is –439.7 kJ

Bond energy (kJ)	**Heat of atomisation (kJ)**
C–H = 143	C = 716.7
C–C = 348	H = 218.0
C=O = 732	O = 249.1
C–O = 351	
O–H = 463	

(a) 200.3 kJ/mole (b) –203.3 kJ/mole (c) 100.3 kJ/mole (d) –100.3 kJ/mole

Soln. Calculate $\Delta H_f(CH_3COOH)$

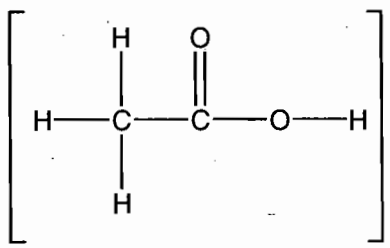
$$2C_{(s)} + 2H_{2(g)} + O_{2(g)} \rightarrow CH_3COOH$$

For reactant:

Heat of atomisation of '2' moles of C = $2\times716.7 = 1433.4$ kJ

Heat of atomisation of '4' moles of H = $4\times218 = 872$ kJ

Heat of atomisation of '2' moles of O = $2\times249.1 = 498.2$ kJ



For products:

Heat of formatin of 3 moles of C—H = $-(3\times413) = -1239$ kJ

Heat of formation of 1 moles of C—C = $-1\times348 = -348$ kJ

Heat of formation of 1 moles of C=C = –732 kJ

Heat of formation of 1 moles of C—O = –351 kJ

Heat of formation of 1 moles of O—H = –468 kJ

Let, resonance energy in $CH_3COOH = x$ kJ

Adding these, we get ΔH_f of CH_3COOH

$-239.4 + x = -439.7$ (given)

$\therefore$ $\boxed{x = -200.3 \text{ kJ/mole}}$

Correct option is (b)

PRACTICE SET

1. The ΔH^0 for the reaction, $C_2H_5OH(\ell) + 3O_2(g) \longrightarrow 3O_2(g) + 3H_2O(\ell)$ is –1, 366.5 kJ. What is the vlaue of ΔU^0
(a) –1, 364 kJ (b) 1, 364 kJ (c) 2, 364 kJ (d) –2, 364 kJ

2. The enthalpy of formation of ethane at 25°C and at consant pressure is –84.68 kJ. The enthalpy of formation at constant volume at this temprature is
(a) 79.70 (b) –79.70 (c) 89.70 (d) –89.70

3. The enthalpy of combustion of C_2H_4 at 17°C and at constant volume is –1389.9 kJ. The enthalpy of combustion at constant pressure is
(a) 1394.7 kJ (b) 1294.7 kJ (c) –1394.7 kJ (d) –1294.7 kJ

4. The enthalpy of neutralization of NH_4OH with HCl is –51.46 kJ mol^{-1}. What is the enthalpy of ioniation of NH_4OH. Assume that the enthalpy of neutralization of a strong acid with a strong base is –57.35 kJ mol^{-1}.
(a) 5.89 kJ mol^{-1} (b) –5.89 kJ mol^{-1} (c) 4.89 kJ mol^{-1} (d) –4.89 kJ mol^{-1}

5. ΔH^0_{neutr} for CH_3COOH with NaOH is –51.63 kJ mol^{-1}. What is the ΔH_{ionize} of CH_3COOH. Assume that the enthalpy of neutralization of a strong acid with a strong base is –57.35 kJ mol^{-1}.
(a) 4.72 kJ mol^{-1} (b) –4.72 kJ mol^{-1} (c) –5.72 kJ mol^{-1} (d) 5.72 kJ mol^{-1}

6. 2 gram of $C_6H_6(g)$ was burnt in excess of oxygen in a bomb calorimeter according to the reaction

$$C_6H_6(g) + 7.5O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(\ell)$$

If the temperature rise is 42.1°C and the heat capacity of the system is 2.0 kJ K^{-1}, the enthalpy of combustion of benzene at constant pressure at 25°C is
(a) –39.20 kJ mol^{-1} (b) 39.20 kJ mol^{-1} (c) –49.20 kJ mol^{-1} (d) 49.20 kJ mol^{-1}

7. For a gaseous reaction at 300K, $\Delta H - \Delta U = -4.98$ kJ, assuming that $R = 8.3JK^{-1}mol^{-1}$, Δn_g is
(a) 1 (b) 2 (c) 3 (d) 4

8. The heat change at constant pressure, q_p, is equal to
(a) ΔU (b) ΔH (c) ΔG (d) RT

9. ΔH^0_f of SO_2 is –297.5 kJ mol^{-1}. The energy required for the decomposition of 32g of SO_2 is
(a) –148.75 kJ (b) 148.75 kJ (c) –297.5 kJ (d) 297.5 kJ

10. For the combustion of one mole of $CH_3COOH(l)$ at 25°C, Δn is
(a) –1 (b) 1 (c) 0 (d) –1/2

ANSWER KEY					
Questions	1	2	3	4	5
Option	(a)	(b)	(c)	(a)	(d)
Questions	6	7	8	9	10
Option	(a)	(b)	(b)	(b)	(c)

Chapter 8

Statistical Thermodynamics

Statistical Thermodynamics

Chemical thermodynamics is a macroscopic view of describing the behaviour of large number of molecules in terms of pressure volume, composition and exchange of heat and work. Whereas Quantum mechanics provides a microscopic description for the structure and interactions of molecules.

Statistical thermodynamics provides the bridge between microscopic mechanics (quantum) and macroscopic thermodynamics (classical).

Types of Statistics:

Different physical situations encountered in nature are described by three types of statistics, the Maxwell-Botzmann (or M-B) statistics, the Bose-Einstein (or B-E) statistics and the Fermi-Dirac (or F-D) statistics. The M-B statistics, developed long before the advent of quantum mechanics, is also called classical statistics whereas the Bose-Einstein statistics and the Fermi-Dirac statistics are collectively called quantum statistics. The characteristics of three types of statistics are summed up as follows:

1. Maxwell-Botlzmann Statistics:

The particles are assumed to be distinguishable and any number of particles may occupy the same energy level. Particles obeying M-B statistics are called boltzons or maxwellons.

Consider a system of N distinguishable particles occupying energy levels $\varepsilon_0, \varepsilon_1, \varepsilon_2$ etc. The total number of arrangements for placing n_0 particles in the ground state energy level ε_0, n_1 particles in the first excited state energy level ε_1, n_2 particles in the second excited state energy level ε_2, and so on, is known as the ***thermodynamic probability***, (***or number of microstates***) W, of the given macrostate. It is, in general, a very large number. Thermodynamics probability W is given by

$$W = \frac{N!}{n_1!n_2!n_3!.....n_j!} = \frac{N!}{\Pi n_i!}$$

where, $N = \Sigma n_i$, N is the total number and summation is over all the energy levels.

The thermodynamic probability for the system of N particles is given by

$$\boxed{W = N!\prod_i \frac{g_i^{n_i}}{n_i!} \times \text{constant}}$$

Where, g_i = degeneracy (or multiplicity) of the energy level ε_i.

It is well known that the entropy S and probability W of a given state of system are related by the Boltzmann equation, the most famous equation in statistical mechanics,

$$\boxed{S = k \ln W}$$

2. **Bose-Einstein Statistics:**

The particles are indistinguishable and any number of particles may occupy a given energy level. This statistics is obeyed by the particles having integral spin, such as hydrogen (H_2) deuterium (D_2), nitrogen (N_2), helium-4 (^4He) and photons. Particles obeying B-E statistics are called bosons.

In Bose-Einstein statistics, we deal with the distribution of indistinguishable particle among the energy levels with no limit on the number of particles in any of the energy state.

The number of ways of placing N indistinguishable particles in g distinguishable energy states with no restriction on the nmber per energy state is given by

$$W = \frac{(g+N-1)!}{(g-1)!N!}$$

The thermodynamic probability of a given distribution of particles over the energy levels is the product of number of arrangements of all energy levels, i.e.

$$W = \Pi_i \frac{(g_i+N_i-1)!}{(g_i-1)!N_i!}$$

3. **Fermi-Dirac Statistics:**

The particles are indistinguishable but only one particles may occupy a given energy level. This statistics is obeyed by particles having half-integral spin, e.g. the protons, electrons, helium-3 (^3He) and nitric oxide (NO). Particles obeying F-D statistics are called **fermions**.

In Fermi-Dirac statistics, we deal with the distribution of indistinguishable particles among the energy levels with only particle in any of the energy state.

Let N indistinguishable identical particles be distributed over g distinguishable degeneracy energy states with the restriction of only one particle in any of energy state. The later condition requires that $N \leq g$.

For distinguishable particles, we will have

g choices for the 1st particle

g–1 choices for the 2nd particle

.....

g – N + 1 choice for the N^{th} particle.

The total choices or arrangements will be

$$(g)(g-1).....(g-N+1) = \frac{g!}{(g-N)!}$$

Since the particles are indistinguishable, the above arrangement has to be divided by N! permutations of the N particles. Hence, the number of ways of placing N indistinguishable particles in g distinguishable degenerate energy states with a limit of no more than one particle per energy state is

$$W = \frac{g!}{(g-N)!N!}$$

The thermodynamics probability of a given distribution of particles over energy levels is the product of number of arrangements of all energy levels, i.e.

$$W = \Pi_i \frac{g_i}{(g_i-N_i)!N!}$$

The expression for the most probable distribution of N particles among the energy levels according to the Fermi-Dirac statistics.

$$\therefore \quad \boxed{n_i = \frac{g_i}{\exp(\alpha + \beta\varepsilon_i) + 1}}$$

Summary for the three types of Statistics:

Statistics	Thermodynamic probability	Number of particles in the ith state	Entropy
Maxwell-Boltzmann	$W_{MB} = N!\prod_i \frac{g_i^{n_i}}{n_i!}$	$n_i = \frac{g_i}{e^{\alpha+\beta\varepsilon_i}}$	$S = k \ln W_{MB}$
Bose-Einstein	$W_{BE} = \prod_i \frac{(N_i + g_i - 1)!}{N_i!(g_i - 1)!}$	$n_i = \frac{g}{e^{\alpha+\beta\varepsilon_i} - 1}$	$S = k \ln W_{BE}$
Fermi-Dirac	$W_{FD} = \prod_i \frac{g_i!}{N_i(g_i - N_i)!}$	$n_i = \frac{g_i}{e^{\alpha+\beta\varepsilon_i} + 1}$	$S = k \ln W_{FD}$

The probability must be a maximum for an equilibrium state so that at equilibrium

$$\boxed{S = k \ln W_{max}}$$

Stirling's Theorem : Stirling's theorem or approximation gives

$\ell n\ n! = n\ \ell n - n$ (Provided n is very large.)

SOLVED PROBLEMS

1. What is the number of ways of distributing 20 identical objects with the arrangements 1, 0, 3, 5, 10, 1.

(a) 9.31×10^{-8} (b) 9.31×10^{8} (c) 93.1×10^{-8} (d) 93.1×10^{8}

Soln. Sine we konw that, $W = \frac{20!}{1!0!3!5!10!1!} = 9.31\times10^{8}$

Correct option is (b)

2. What is the weight of the configuration in which 20 objects are distributed in the arrangement 0, 1, 5, 0, 3, 2,0, 1, 0, 8.

(a) 4.19×10^{10} (b) 4.19×10^{12} (c) 4.19×10^{14} (d) 4.19×10^{16}

Soln. Sine we konw that, $W = \frac{20!}{0!1!5!0!3!2!0!1!0!8!} = 4.19\times10^{10}$

Correct option is (a)

3. (a) In how many ways (W) can six distinguishable molecules be placed in three different energy levels with 3 molecules in the first level, two in the second and one in the third.
(b) Write down the different ways of distribution of three balls a, b, c between two boxes

Soln. (a) $W = \frac{6!}{3!2!1!} = \frac{720}{12} = 60$

(b) The eight different distributions are $\frac{abc}{0}, \frac{ab}{c}, \frac{ac}{b}, \frac{bc}{a}, \frac{0}{abc}, \frac{c}{ab}, \frac{b}{ac}, \frac{a}{bc}$

4. The number of configurations in the most probable state, according to Boltzmann formula, is

(a) e^{S/k_B} (b) e^{-S/k_B} (c) e^{-E/k_BT} (d) $e^{-\Delta G/k_BT}$ **[NET June 2014]**

Soln. Since we know that, $S = k_B \ell nW$

$S / k_B = \ell nW$

$W = e^{S/k_B}$

Correct option is (a)

5. Using Boltzmann distribution, the probability of an oscillator occupying the first three levels (n=0, 1 and 2) found to be $p_0 = 0.633$, $p_1 = 0.233$ and $p_2 = 0.086$.

The probability of finding an oscillator in energy levels in $n \geq 3$ is

(a) 0.032 (b) 0.048 (c) 0.952 (d) 1.000

Soln. Total probability $= P_T = 1$

Probability of occupying first three levels $= P_0 + P_1 + P_2$

$P_T = P_0 + P_1 + P_2 +$ probability of finding an oscillator in energy levels in $n \geq 3$

$1 = 0.952 + P_{n\geq 3} = 1 - 0.952 = 0.048$

Correct answer is (b)

6. The number of ways in which four molecules can be distributed in two different energy levels is

(a) 6 (b) 3 (c) 16 (d) 8

Soln. Number of energy levels $(g_i) = 2$

Number of molecules $(N_i) = 4$

The number of ways of distribution $= g_i^{N_i} = 2^4 = 16$

(since, it is not given either particles are distinguisable or indistinguishable, therefore, we will consider it a distinguishable)

Correct option is (c)

Canonical Ensemble Partition Function:

If g_i be the weight factor for the i^{th} level, then

$$n_i = g_i\, e^{-\alpha}.e^{-\beta\epsilon_i} \quad \Rightarrow n_i = e^{-\alpha}.\Sigma\left(g_i.e^{-\beta\epsilon_i}\right)$$

Where α and β are constant and $\beta = 1/kT$.

According to Boltzmann distribution law, $\dfrac{n_i}{n} = \dfrac{g_i\, e^{-\epsilon_i/kT}}{\Sigma g_i\, e^{-\epsilon_i/kT}}$

the factor in denominator $\Sigma g_i\, e^{-\epsilon_i/kT}$ is called ***partition function*** denoted by q.

Thus, $\dfrac{n_i}{n} = \dfrac{g_i\, e^{-\epsilon_i/kT}}{q} \quad \Rightarrow \boxed{n_i = n g_i \dfrac{e^{-\epsilon_i/kT}}{q}}$

Thus partition function is the sum of the probability factor for different energy levels or 'the number of ways in which energy of a system is distributed among the molecules constituting the system.'

Thus the partition function can be expressed

$$\boxed{q = \Sigma g_i\, e^{-\epsilon_i/kT}}$$

The energy E_i of a system containing non-interacting particles a, b, c ..... is given by

$$E_i = \epsilon_1(a) + \epsilon_2(b) + \epsilon_3(c) + \ldots\ldots\ldots + \epsilon(N)$$

The partition function q_c is defined as (for $g_i = 1$)

$$q_c = \sum_i e^{(-E_i/kT)}$$

Since, a, b, c etc are identical therefore, each particle will have same set of energies and as well as partition function, $\Rightarrow q_a = q_b = q_c = \ldots\ldots\ldots = q_N$

Therefore, for a system of N independent molecules the canonical ensemble partition function is given by

$$\boxed{q_c = q^N \text{ (for distinguishable entities)}}$$

The relation is applicable for the systems of a perfect crystal.

In the case of a gas the molecules are indistinguishable. Therefore the energy states that differ by the two particles are not distinguishable and should be counted only once:

$$E_1 = \epsilon_1(a) + \epsilon_2(b) + \ldots\ldots\ldots\text{states}$$

$$E_2 = \epsilon_2(b) + \epsilon(a) + \ldots\ldots\ldots\text{states}$$

Therefore the partition function for an ideal gas is:

$\boxed{q_c = q^N / N!}$ For indistinguishable molecules

Physical significance of partition function (q) :

(i) It indicates how the particles are distributed among the various energy levels.

(ii) It reflects the diversity of energy states of the molecules of a system.

(iii) It determines the relative population of any two quantum states p and q by the ratio n_p/n_q.

We can derive the ratio as

$$\boxed{\frac{n_p}{n_q} = \left(\frac{g_p}{g_q}\right) e^{-(\epsilon_p - \epsilon_q)/kT}}$$

Since partition function for a molecule is a function of temperature and since the exponents in $e^{-\epsilon/kT}$ are inversely proportional to the temperature, the terms in partition function approach zero as $T \to 0$ except for one which is $g_0 e^{-\epsilon_0/kT}$ for the ground state because $\epsilon_0 = 0$ so that this term is equal to g_o. Thus as $T \to 0$ q approaches the degeneracy of the ground state.

As $T \to \infty$, $\frac{\epsilon_i}{kT} \to 0$, so that $e^{-\epsilon_i/kT}$ approaches unity and q approaches the sum of degenercies of the levels is $\boxed{q = \Sigma g_i}$.

Problem : When $T \to \infty$, value of the single-particle partition function will be (given : degeneracy of level $j = g_j$) **[CSIR DEC. 2014]**

(a) 1 (b) g_0 (c) $\Sigma_j g_j$ (d) $\frac{1}{\Sigma_j g_j}$

Soln. Correct option is (c)

Translational Partition Function:

The particle can execute translational motion along x, y and z directions. The translational partition function for a molecules along x, y and z axis is given by

$$q_t(x) = \Sigma g_t e^{-\epsilon_{t(x)}/kT};\ q_t(y) = \Sigma g_t e^{-\epsilon_{t(y)}/kT};\ q_t(z) = \Sigma g_t e^{-\epsilon_{t(z)}/kT}$$

where ϵ_t is the translational energy, k is Boltzmann constant and g_t is statistical weight factor.

Hence the net translational partition function of a molecule will be

$$q_t = q_t(x)\,q_t(y)\,q_t(z)$$

Since $g_t = 1$ for each level

$$\therefore \quad q_t(x) = \Sigma e^{-\epsilon_t/kT} \text{ and so on.}$$

Now in a box of sides l_x, l_y and l_z.

$$\epsilon_{t(x)} = \frac{n^2h^2}{8m\ell_x^2} \text{ and so on}$$

$$\therefore \quad q_{t(x)} = \Sigma\, e^{\left(-n^2h^2/8m\ell_x^2\, kT\right)}$$

Or, $$q_{t(x)} = \frac{(2\pi mkT)^{1/2}}{h} \text{ and so on}$$

Hence the net translational partition function of molecule will be

$$q_t = \frac{(2\pi mkT)^{3/2}}{h^3}\left(\ell_x, \ell_y, \ell_z\right)$$

But volume of box $(V) = \ell_x, \ell_y, \ell_z$

Hence, $$q_t = \frac{(2\pi mkT)^{3/2}}{h^3} \times V$$

Since q_t for a molecule is proportional to the voluem V in which it moves. Therefore, q_t is an extensive variable

The quantity $\left(h^2/2\pi mkT\right)^{1/2}$ is called thermal wavelength (Λ). Thus

$$\boxed{q_t = \frac{V}{\Lambda^3}}$$

The condition for the applicability of Boltzmann statistics is that thermal wavelength must be small compare mean distance between molecules.

Rotational Partition Function:

Rotational energy (ϵ_r) for a diatomic molecule in J^{th} rotational energy level is given by

$$\epsilon_r = j(j+1)\,h^2/8\pi^2 I$$

where j is rotational quantum number and I is moment of inertia.

The degenercy of j^{th} rotational level will be 2j+1 and is equal to rotational statistical weight factor (g).
The rotational partition function for a diatomic molecule will be

$$q_r = \Sigma g_r\, e^{-\epsilon_r/kT}$$

Thus $$q_r = \Sigma(2j+1)e^{\left[-j(j+1)h^2/8\pi^2 IkT\right]}$$

Which on solving we obtain

$$\boxed{q_r = \frac{8\pi^2 IkT}{h^2} = \frac{T}{\theta_r}}$$

Where $\theta_r = \frac{h^2}{8\pi^2 Ik}$ is rotational temperature.

This equation is for heteronuclear diatomic molecules like NO, HCl etc.

For homonuclear diatomic molecules

$$\boxed{q_r = \frac{8\pi^2 IkT}{2h^2}}$$

In general, $$\boxed{q_r = \frac{8\pi^2 IkT}{\sigma h^2}}$$

Where, σ is symmetry number and σ is 2 for homonuclear diatomic molecules.

For nonlinear polyatomic molecules

$$\boxed{q_r = \frac{8\pi^2 (I_A I_B I_C)^{1/2} (kT)^{1/2}}{\sigma h^3}}$$

Where I_A, I_B, I_C are moment of inertia about three principal axis.

Quantum Mechanical explanation of symmetry number

The total wave function of a molecule is given by

$$\psi_{total} = \psi_t \psi_r \psi_v \psi_e \psi_n$$

where the subscripts t, r, v, e and n stand for transitional rotational, vibrational, electronic and nuclear, respectively.

On the basis of the nuclear spin quantum number, the atom are two types:

(i) Boson: The nuclei of these atom have integral spin quantum number.

e.g. ^2H (I = 1), ^{14}N (I = 1) and ^{10}B(I = 3)

For bosons, the total wave function is symmetric.

(ii) Fermions : The nuclei of these atom have half-integral spin quantum number.

e.g. $^1H\left(I=\frac{1}{2}\right)$; $^{15}N\left(I=\frac{1}{2}\right)$; $^{17}O\left(I=\frac{5}{2}\right)$ and $^{35}Cl\left(I=\frac{3}{2}\right)$

For fermions, the total wave function is antisymmetric.

- The rotational wave functions have the same symmetry characteristics as those of the angular functions of the hydrogen atom

  ψ_r are symmetric for even values of rotational quantum number J.

  ψ_r are antisymmetric for odd values of rotational quantum number J.
- A nucleus with spin quantum number I has a total of 2I + 1 spin states. These states are represented by the magnetic spin quantum number which have values of +I, +(I–1), ... – (I–1), –I.

For example, for a proton $\left(I=\frac{1}{2}\right)$ the two states are,

$m_I = +\frac{1}{2}$, known as α spin. Its wave function is represented by the symbol α.

$m_I = -\frac{1}{2}$, known as β spin. Its wave function is represented by the symbol β.

A diatomic molecule involving identical nuclei with spin quantum number I, has a total of $(2I + 1)^2$ nuclear wave functions. Out of these wave functions,

$(2I+1)^2$ (2I)/2 i.e. I(2I+1) wave functions are antisymmetric.
and $(2I+1)^2 - I(2I+1)$, i.e. (I + 1) (2I+1) wave functions are symmetric.

Example: In hydrogen molecule, we have three symmetric nuclear spin wave functions. These are $\alpha\alpha$, $\beta\beta$ and $\left(\frac{1}{\sqrt{2}}\right)(\alpha\beta+\beta\alpha)$.

One antisymmetric nuclear spin wave function. This is $\left(\frac{1}{\sqrt{2}}\right)(\alpha\beta-\beta\alpha)$.

Factor affecting symmetry of total wave function:

(1) For bosons, the total wave function has to be symmetric. This is possible when I(2I+1) antisymmetric nuclear spin functions couple with antisymmetric rotational wave functions for which rotation quantum number J has ***odd*** values. (I + 1) (2I + 1) symmetric nuclear spin functions couple with symmetric rotational wave functions for which rotational quantum number J has ***even*** values.

(2) For fermions, the total wave function has to be antisymmetric. This is possible only when I(2I+1) antisymmetric nuclear spin functions couple with symmetric rotational wave functions for which rotational quantum number J has **even** values. (I + 1) (2I + 1) symmetric nuclear spin functions couple with antisymmetric rotational wave functions for which rotational quantum number J has **odd** values. These are also applicable to linear polyatomic molecules such as CO_2 and C_2H_2.

Expressions of partition functions:

For Bosons, we have

$$q_{r,n} = (I+1)(2I+1)\sum_{J\,(\text{even})}(2J+1)\,e^{-J(J+1)h^2/8\pi^2 IkT} + I(2I+1)\sum_{J\,(\text{odd})}(2J+1)\,e^{-J(J+1)h^2/8\pi^2 IkT} \quad \ldots (i)$$

For fermions, we have

$$q_{r,n} = (I+1)(2I+1)\sum_{J\,(\text{odd})}(2J+1)\,e^{-J(J+1)h^2/8\pi^2 IkT} + I(2I+1)\sum_{J\,(\text{even})}(2J+1)\,e^{-J(J+1)h^2/8\pi^2 IkT} \quad \ldots (ii)$$

The heat capacity of hydrogen gas :

Rotational partition function:

For hydrogen atom, $I=\frac{1}{2}$, hence from equation (ii), we obtain that,

$$q_{r,n} = (1)\sum_{J\,(\text{even})}(2J+1)\,e^{-J(J+1)h^2/8\pi^2 IkT} + (3)\sum_{J\,(\text{odd})}(2J+1)\,e^{-J(J+1)h^2/8\pi^2 IkT}$$

Ortho and para hydrogens:

The hydrogen molecule with opposite nuclear spin (i.e. antisymmetric nuclear spin function) is called para hydrogen. It is associated with rotational wave functions having only even values of rotational quantum numbers.

The hydrogen molecule with parallel nuclear spin (i.e. symmetric nuclear spin function) is called ortho hydrogen. It is associated with rotational wave functions having only odd values of rotational quantum numbers.

The ratio of molecules of ortho and para dihydrogen is given by

$$\frac{N_{ortho}}{N_{para}} = \frac{(3)\sum_{\text{odd J}}(2J+1)\,e^{-J(J+1)h^2/8\pi^2IkT}}{(1)\sum_{\text{even J}}(2J+1)\,e^{-J(J+1)h^2/8\pi^2IkT}}$$

This ratio depends on the temperature of the system. The percentage of para dihydrogen is 100 at 0K. It decreases with increase in temperature and attains a value 25 percent at high temperatures.

Effect of nuclear spin:

The effect of nuclear spin is important in case of homonuclear di-atomic molecules such as the two isotopes of hydrogen atom (H_2 and D_2). In case of heteronuclear diatomic molecules, the effect of nuclear spin is not so important.

Let us consider a homonuclear diatomic molecule where each of its constitutent atom has spin quantum number *i*. Hence the resultant spin quantum number I of the molecule can assume the values ranging from 0 to (2 *i*) in steps of unity. For a half integer spin *i*, total nuclear spin I can be odd or an even integer, and the relative nuclear partition functions for even and odd values of I are

$$Z'_{even} = \frac{i}{2i+1} \qquad Z'_{odd} = \frac{i+1}{2i+1}$$

For an integer spin *i*, total nuclear spin I can be an odd or an even integer, and the relative nuclear partition functions for even and odd values of I are

$$Z'_{even} = \frac{i+1}{2i+1} \qquad Z'_{odd} = \frac{i}{2i+1}$$

Taking into account the nuclear spin effect, the rotational partition function for such molecules can be modified to

$$\boxed{Z_{rot} = \left(2Z'_{even}\,Z_{even} + Z'_{odd}\,Z_{odd}\right)}$$

Where, $Z_{even} = \sum_{J=0,2,4}(2J+1)\exp\left[-\sigma_r J(J+1)\right]$

$$Z_{odd} = \sum_{J=1,3,5}(2J+1)\exp\left[-\sigma_r J(J+1)\right]$$

At high temperatures, $Z_{even} \cong Z_{odd} \cong \frac{1}{2}Z_{rot} = (kT/2B)$. It shows that at high temperature, the free energy, entropy, internal energy and specific heat of a diatomic molecules does not depend on the nature of the atoms in the molecule. At low temperatures, the situation is different and the gas may be regarded as a combination of two components corresponding to even and odd values of total spin quantum number.

For hydrogen isotopes, the molecules with greater nuclear statistical weight are termed as ortho-hydrogen molecules, whereas those with smaller weight are known as para-hydrogen molecules. Thus, for H_2 and D_2, the nuclear partition functions are as follows:

$$\boxed{H_2\left(i=\frac{1}{2}\right)\begin{cases}\text{ortho} & Z'_{odd} = \dfrac{1/2+1}{2} = \dfrac{3}{4}\end{cases}}\;;\qquad \boxed{D_2(i=1)\begin{cases}\text{ortho} & Z'_{even} = \dfrac{2}{3}\\ \text{para} & Z'_{odd} = \dfrac{1}{3}\end{cases}}$$

The relative abundances of the two species in equilibrium are determined by the relative magnitude of the two parts of the partition function Z_{rot}. Thus, the ortho-para ratio is given by

$$\frac{N(\text{ortho}-H_2)}{N(\text{para}-H_2)}=\frac{Z'_{odd}\,Z_{odd}}{Z'_{even}\,Z_{even}}=\frac{3\,Z_{odd}}{Z_{even}}$$

$$\frac{N(\text{ortho}-D_2)}{N(\text{para}-D_2)}=\frac{Z'_{even}\,Z_{even}}{Z'_{odd}\,Z_{odd}}=\frac{2\,Z_{even}}{Z_{odd}}$$

As $T\to 0$, all the molecules tend to be in the lowest rotational state with J = 0, and thus the H_2 gas is only para whereas the D_2 gas is only ortho. At high temperatures, $Z_{even}\cong Z_{odd}$, the abundance ratio for H_2 is three and for D_2 is two. Hence, as the temperature varies from zero to infinite, the ratio varies from zero to three for H_2 and from zero to two for D_2. However, for all practical purposes, we use the ratio 3 and 2, respectively. The densities of the molecules can be expressed as

$$N_{H_2}=\frac{3}{4}N_{ortho}+\frac{1}{4}N_{para}$$

$$N_{D_2}=\frac{2}{3}N_{ortho}+\frac{1}{3}N_{para}$$

Accordingly, the specific heat is

$$(c_{rot})_{H_2}=\frac{3}{4}c_{ortho}+\frac{1}{4}c_{para}$$

$$(c_{rot})_{D_2}=\frac{2}{3}c_{ortho}+\frac{1}{3}c_{para}$$

Vibrational Partition Function:

The partition function for vibrational energy of a diatomic molecule is $q_v=\Sigma g_v e^{-\epsilon_v/kT}$

where g_v = statistical weight factor for vibration, vibrational energy of a diatomic molecule is $\epsilon_v=\left(v+\frac{1}{2}\right)h\upsilon_0$

v is vibrational quantum number with values 0,1, 2,.....∞. υ_0 is fundamental frequency of vibration. Since g_v is unity for each energy level, we may express

$$q_v=\Sigma\, e^{-\epsilon_v/kT}$$

Thus, vibrational partition function can be expressed as

$$q_v=\sum_{V=0}^{\infty} e^{-\left(v+\frac{1}{2}\right)h\upsilon_0/kT}$$

On solving above expression, we get

$$q_v=e^{\frac{-h\upsilon_0}{2kT}}\times\left(1-e^{-h\upsilon_0/kT}\right)^{-1} \quad \text{or} \quad q_v=\frac{e^{\frac{-h\upsilon_0}{2kT}}}{1-e^{-h\upsilon_0/kT}} \quad \text{or} \quad q_v=\frac{1}{2\sinh\left(\frac{h\upsilon_0}{2kT}\right)}$$

If ground state energy is zero $\left(v+\frac{1}{2}=v\right)$ then

$$q_v=\frac{1}{1-e^{\frac{h\upsilon_0}{kT}}} \text{ or } q_v=\left(1-e^{-\frac{h\upsilon_0}{kT}}\right)^{-1}$$

For most diatomic molecules at ordinary temperature the value of q_v is nearly unity because $h\upsilon_0$ is appreciably greater than kT.

Electronic Partition Function:

The electronic partition function can be expressed as

$$q_e = \Sigma g_e\, e^{-\epsilon_e/kT}$$

where, ϵ_e = electronic energy of molecule.

g_e = electronic statistical wt factor.

In general $g_e = 2j + 1$

Where j is total angular momentum and its values are denoted by symbols $S_{1/2}$, $P_{1/2}$, $P_{3/2}$ where the subscript equals J. Thus

$$q_e = \Sigma(2j+1)e^{-\epsilon_e/kT}$$

The value of q_e may exceed unity because of degeneracy. For example, O_2 has two unpaired electrons in the ground state and is triply degenerate ($g_e = 3$). Hence

$$q_e = \Sigma g_e\, e^{-\epsilon_e/kT} = \Sigma 3.e^{-0/kT} = 3 \qquad (\because e^0 = 1)$$

For atoms and molecules with one unpaired electron spin degeneracy is 2 in ground state.

Hence, $q_e = \Sigma 2.\, e^{-0/kT} = 2$

Generally the electronic energy acquired by the molecule at ordinary temperatured is extremely low so its contribution to the net partition function is immaterial.

Remark: The energy term ϵ represents the total energy of the molecule such as translational, (ϵ_t), rotational (ϵ_r), vibrational (ϵ_v), electronic (ϵ_e) and zero point energy (ϵ_0) is

$$\epsilon = \epsilon_t + \epsilon_r + \epsilon_v + \epsilon_e + \epsilon_0 + \epsilon_{nuc.}$$

Also the statistical wt factor is defined as

$$g = g_t \times t_r \times g_v \times g_e \times g_0 \times g_{nuc}$$

Thus partition function becomes

$$q = \Sigma(g_t \times g_r \times g_v \times g_e \times g_0 \times g_{nuc.}) \times e^{-[\epsilon_t+\epsilon_r+\epsilon_v+\epsilon_e+\epsilon_0+\epsilon_{nuc}]/kT}$$

Or, $$q = \Sigma g_t\, e^{-\epsilon_t/kT} \times \Sigma g_r\, e^{-\epsilon_r/kT} \times \Sigma g_v\, e^{-\epsilon_{v/kT}} \times \Sigma g_e\, e^{-\epsilon_e/kT} \times \Sigma g_0 e^{-\epsilon_0/kT} \times \Sigma g_{nuc} e^{-\epsilon_{nuc}/kT}$$

Or, $$\boxed{q = q_t \times q_r \times q_v \times q_e \times q_0 \times q_{nuc.}}$$

Thus net partition function is the product of the separate partition functions with respect to different types of energies associated with the molecules.

Relation between Partition function and thermodynamic functions:

1. **Internal Energy:** If E is internal energy of the system at temperature T and Q is the partition function of the particles in the system. Then the expression for their relationship is

$$\boxed{E = kT^2\left(\frac{\partial \ell n q^N}{\partial T}\right)_V} \text{ or } \boxed{E = NkT^2\left(\frac{\partial \ell n q}{\partial T}\right)_V}$$

For N molecules of the system.

For 1 mole of the system

$$E = N_A kT^2 \left(\frac{\partial \ell nq}{\partial T}\right)_V = RT^2 \left(\frac{\partial \ell nq}{\partial T}\right)_V$$

2. Heat capacity:

$$\because \quad E = RT^2 \left(\frac{\partial \ell nq}{\partial T}\right)_V$$

$$\Rightarrow \quad \left(\frac{\partial E}{\partial T}\right)_V = \frac{\partial}{\partial T}\left[RT^2 \left(\frac{\partial \ell nq}{\partial T}\right)_V\right] \qquad \text{... (i)}$$

Since, we know that

$$\left(\frac{\partial E}{\partial T}\right)_V = C_V$$

So, from equation (i)

$$\boxed{C_V = \frac{\partial}{\partial T}\left[RT^2 \left(\frac{\partial \ell nq}{\partial T}\right)_V\right]} \qquad \text{... (ii)}$$

$$\therefore \quad C_P - C_V = R$$

$$C_P = R + C_V$$

From equation (ii), we get

$$\boxed{C_P = R + \frac{\partial}{\partial T}\left[RT^2 \left(\frac{\partial \ell nq}{\partial T}\right)_V\right]}$$

3. Entropy and partition function:

For a system containing n molecules at temperature T entropy is related with partition function as

$$\boxed{S = -kn\left[-\ell n\left(\frac{q}{n}\right) + T\left(\frac{\partial \ell nq}{\partial T}\right)_V + 1\right]}$$

And for 1 mole of an ideal gas,

$$\boxed{S = k\left[\ell n(q) + T\left(\frac{\partial \ell nq}{\partial T}\right)_V + 1\right]}$$

In another form, the relation, between entropy (for 1 mole) and partition function is:

$$\boxed{S = k\ell n\left(\frac{q^N}{N!}\right) + kT\left(\frac{\partial \ell nq}{\partial T}\right)_V}$$

4. Work function (A) and partition function:

Since $A = E - TS$

puttng the values of E and S for 1 mole of an ideal gas, we obtain

$$\boxed{A = RT^2 \left(\frac{\partial \ell nq}{\partial T}\right)_V - RT\ell n\left(\frac{q}{N}\right) - RT^2 \left(\frac{\partial \ell nq}{\partial T}\right) - RT}$$

SOLVED PROBLEMS

1. What is the vibrational contribution to the molar heat capacity of $N_2(g)$ at 1000 K. The vibration temperature of $N_2(g)$ is 3374 K.

(a) $4.48 JK^{-1} mol^{-1}$ (b) $3.48 JK^{-1} mol^{-1}$ (c) $5.38 JK^{-1} mol^{-1}$ (d) $6.25 JK^{-1} mol^{-1}$

Soln. Since we know that,

$$C_{V(vib)} = R\left(\frac{\theta_{vib}}{T}\right)^2 \frac{e^{-\theta_{vib}/T}}{\left(1-e^{-\theta_{vib}/T}\right)^2}$$

$$= 8.314\left(\frac{3374}{1000}\right)^2 \frac{e^{-3.374}}{\left(1-e^{-3.374}\right)^2} = 3.48\ JK^{-1}\ mol^{-1}$$

Correct option is (b)

2. What is the fraction of $N_2(g)$ molecules in the $v=0$ and $v=1$ vibrational states at 300K. θ_{vib} of N_2 is 3374 K.

(a) 1.31×10^{5} (b) 1.31×10^{4} (c) 1.31×10^{3} (d) 1.31×10^{2}

Soln. Since we first calculate, $e^{-(\theta_{vib}/T)} = e^{-3374/300} = e^{-11.25} = 1.31\times10^{-5}$

Therefore, $f_0 = 1-e^{-\theta_{vib}/T} \approx 1$ and $f_1 = \left(1-e^{-\theta_{vib}/T}\right)e^{-\theta_{vib}/T} = 1\times1.31\times10^{-5} = 1.31\times10^{5}$

Correct option is (a)

3. The characteristic rotational temperature θ_r for $H_2(g)$ is 87.5 K. What is the value of the molecular partition function for rotation at 3000K?

(a) 17.14 (b) 15.26 (c) 18.21 (d) 19.20

Soln. Since we know that,

$$q_r = \frac{T}{\sigma\theta_r} = \frac{3000K}{2\times87.5K} = 17.14$$

Correct option is (a)

4. The translational partition function of a H atom is 7.8×10^{30} at 3000K in a volume of 0.25 m^3. What is thermal wavelength?

(a) 3.175×10^{-10} m (b) 3.175×10^{-11} m (c) 3.175×10^{-12} m (d) 3.175×10^{-13} m

Soln. Since we know that,

$$\text{Thermal wavelength, } \Lambda = \left(\frac{V}{q_t}\right)^{1/3} = \left(\frac{0.25}{7.8\times10^{30}}\right)^{1/3} = 3.175\times10^{-11}\text{m}$$

Correct option is (b)

5. What is the vibrational partition function for Br_2 at 300 K if the vibrational frequency is 151.2 cm^{-1}.

(a) 0.725 (b) 7.25 (c) 1.94 (d) 19.4

Soln. $q_V = \frac{1}{1-e^{-h\upsilon_0/kT}}$ ... (i)

$$\frac{h\upsilon_0}{kT}=\frac{hc\omega}{kT}=\frac{6.62\times10^{-34}\times3\times10^{10}\times151.2}{1.38\times10^{-23}\times300}=0.725$$

From equation (i), we get

$$q_v=\frac{1}{1-e^{0.725}}=1.94$$

Correct option is (c)

6. (a) What is the electronic partition function of Cl atom if it is assumed that energies of ist and higher excited states are very large.

(a) 4 (b) 3 (c) 6 (d) 7

(b) If energy of the first excited state of Cl atom is 0.11 eV, what is the contribution to the partition function of this term at 1000 K.

(a) 5.56 (b) 4.56 (c) 7.32 (d) 8.56

Soln. (a) The ground state spectroscopic term for Cl is $^2P_{3/2}$ where subscript is the value of J.

The degeneracy of any states is (2J+1). Thus

$$g_0=2J+1=2\times\frac{3}{2}+1=4$$

$$q_e=g_0(\text{elec})=4$$

Correct option is (a)

(b) The J values for first excited state is $\left(^2P_{1/2}\right)$ is 1/2,

So, $g_1=2J+1=2\times\frac{1}{2}+1=2$

$$q_e=g_0+g_1\,e^{(-\epsilon/kT)}=4+2e^{\left(\frac{-1.8\times10^{-20}J}{1.38\times10^{-23}\times1000}\right)}=4.56$$

Correct option is (b)

7. What is the rotational partition function of H_2 molecule at 300K. Moment of inertia of H_2 molecule is 4.59×10^{-47} kg m^2, symmetry number $\sigma=2$.

(a) 19.20 (b) 18.20 (c) 17.20 (d) 15.20

Soln. $$q_r=\frac{8\pi^2IkT}{\sigma h^2}=\frac{8\times(3.14)^2\times4.59\times10^{-47}\times1.38\times10^{-23}\times300}{2\times\left(6.626\times10^{-34}\right)^2}=17.20$$

Correct option is (c)

8. What is the molar residual entropy of a crystal in which the molecules can adopt 6 orientations of equal ene at 0K.

(a) 14.89 JK^{-1}mol^{-1} (b) 13.89 JK^{-1}mol^{-1} (c) 16.89 JK^{-1}mol^{-1} (d) 12.89 JK^{-1}mol^{-1}

Soln. The residual entropy is given by $S=Nk\ell nW$

W = number of orientations, N = number of particles = N_A = 1 mol

$N_Ak=R=$ Gas constant.

$=8.314$ JK^{-1} mol^{-1}.

$$S=R\ell n6=8.314\times2.303\log6=14.89\text{ JK}^{-1}\text{mol}^{-1}$$

Correct option is (a)

9. Assuming H_2 and HD molecules having equal bond length. What is the ratio of the rotational partition functions of these molecules at temperature above 1000 K?

(a) $\frac{5}{3}$ (b) $\frac{2}{8}$ (c) $\frac{8}{3}$ (c) $\frac{3}{8}$

Soln. $q_r = \frac{8\pi^2 IkT}{\sigma\hbar^2} \Rightarrow q_r \propto \frac{I}{\sigma}$ or $\frac{\mu r^2}{\sigma}$ or $q_r \propto \frac{\mu}{\sigma}$

$$\frac{q_{H_2}}{q_{HD}} = \frac{\frac{1\times1}{1+1}}{\frac{1\times2}{1+2}} \times \frac{1}{2} \Rightarrow \frac{q_{H_2}}{q_{HD}} = \frac{\frac{1}{2}}{\frac{2}{3}} \times \frac{1}{2} = \frac{3}{4} \times \frac{1}{2} = \frac{3}{8}$$

Correct option is (d)

10. What is the translational partition function of a H_2 molecule confined in a 100 ml flask at 1298 K. [Given : Molecular wt. of $H_2 = 2.016$.]

(a) 2.8×10^{26} (b) 2.8×10^{-26} (c) 28×10^{26} (d) 28×10^{-16}

Soln. Since, we know that,

$$q_t = \frac{(2\pi mkT)^{3/2}}{h^3} \times V = \sqrt{M^3T^3} \times V \times 1.89\times10^{26}$$

$$= \sqrt{2.016^3 \times 298^3} \times 100\times10^{-4} \times 1.89\times10^{26} = 2.8\times10^{26}$$

Correct option is (a)

11. The first excited state of Cl atom $^2P_{1/2}$ lies at 0.11 eV above the ground state $^2P_{3/2}$. What is the electronic partition function of Cl atom at 1000K.

(a) 5.26 (b) 4.56 (c) 6.18 (d) 7.18

Soln. For the ground state $g_0 = 2j+1 = 2\times\frac{3}{2}+1 = 4$

For the first excited state $g_1 = 2\left(\frac{1}{2}\right)+1 = 2$

Hence at 1000K, $q_e = g_0e^{-\epsilon_0/kT} + g_1e^{-\epsilon_1/kT} = 4e^0 + 2e^{\frac{0.11\times1.6\times10^{-19}}{1.38\times10^{-23}\times1000}} = 4+2(0.28) = 4.56$

Correct option is (b)

12. For H_2 gas at 3000 K, what is the vibrational temperature θ_{vib} and the vibrational partition function q_{vib}, respectively, given that the fundamental vibrational frequency of H_2 molecule is 4405.3 cm^{-1}.

(a) 6338K, 1.137 (b) 7456K, 1.137 (c) 6338K, 2.234 (d) 7456K, 2.234

Soln. $q_{vib} = \frac{h\upsilon}{K} = \frac{hc\bar{\upsilon}}{K} = \frac{6.626\times10^{-34}\times3\times10^8\times4.4053\times10^2}{1.38\times10^{-23}} = 6338.3K$

$$q_{vib} = \frac{1}{1-e^{-\theta/T}} = \frac{1}{1-e^{-6338.3/3000}} = \frac{1}{1-e^{-2.1128}} = \frac{1}{1-0.1210} = \frac{1}{0.879} = 1.137$$

Correct option is (a)

13. Give the symmetry number for each of the following molecules

(a) CO (b) O_2 (c) CO_2 (d) H_2S (e) O_3 (f) SO_3 (g) SiH_4
(h) $CHCl_3$ (i) SF_6 (k) Al_2Cl_6

Soln. For homonuclear diatomic molecule or a symmetrical linear molecule symmetry number $\sigma = 2$ and for hetero nuclear diatomic molecule $\sigma = 1$.

(a) CO $\rightarrow$ $\sigma = 1$
(b) O_2 $\rightarrow$ $\sigma = 2$
(c) CO_2 $\rightarrow$ $\sigma = 1$
(d) H_2S $\rightarrow$ $\sigma = 2$
(e) O_3 $\rightarrow$ $\sigma = 2$
(f) SO_3 $\rightarrow$ $\sigma = 6$
(g) SiH_4 $\rightarrow$ $\sigma = 12$
(h) $CHCl_3$ $\rightarrow$ $\sigma = 3$
(i) SF_6 $\rightarrow$ $\sigma = 24$
(k) Al_2Cl_6 $\rightarrow$ $\sigma = 4$

14. The energies of first three energy levels of fluorine atom are as follows

Energy level	**Energy (cm^{-1})**
$^2P_{3/2}$	0.0
$^2P_{1/2}$	404.0
$^2D_{5/2}$	102406.5

Calculate:

(i) Electronic partition function and
(ii) The fraction of fluorine atoms in the three energy levels at 1000 K.

Soln. $g_0 = 2\times 3/2 + 1 = 4;\ g_1 = 2\times 1/2 + 1 = 2;\ g_2 = 2\times 5/2 + 1 = 6$

$$q_e = g_0 e^{-\epsilon_0/kT} + g_1 e^{-\epsilon_1/kT} + g_2 e^{-\epsilon_2/kT} = 4\times e^0 + 2e^{-404\hbar c/kT} + 6e^{-102406.5\hbar c/kT}$$

$$= 4 + 2e^{-0.5813} + 6e^{-147.4} = 5.118$$

(ii) From Maxwell Boltzmann distribution.

$$n_i = \frac{Ng_i e^{-\epsilon_i/kT}}{q_{el}}$$

$$\frac{n_0}{N} = \frac{g_0 e^{-\epsilon_0/kT}}{g_{el}} = \frac{4\times 1}{5.118} = 0.72$$

$$\frac{n_1}{N} = \frac{g_1 e^{-\epsilon_1/kT}}{q_{el}} = \frac{2\times e^{-0.5813}}{5.118} = 0.218$$

$$\frac{n_2}{N} = \frac{g_2 e^{-\epsilon_2/kT}}{q_{el}} = \frac{6\times e^{-147.4}}{5.118} = 0$$

15. N non-interacting molecules are distributed among three non-degenerate energy levels $\varepsilon_0 = 0, \varepsilon_1 = 1.38\times10^{-21}\,J$ and $\varepsilon_2 = 2.76\times10^{-21}\,J$, at 100K. If the average total energy of the system at this temperature is $1.38\times10^{-18}\,J$, the number of molecules in the system is: **[GATE 2007]**

(a) 1000 (b) 1503 (c) 2354 (d) 2987

Soln. Since, $\frac{n_1}{n_0} = e^{-[E_2-E_0]/kT}$

$$\frac{n_1}{n_0} = e^{-\left[1.38\times10^{-21}-1.38\times10^{-21}\right]/kT}$$

$$\Rightarrow \quad \frac{n_1}{n_0} = e^0 = 1$$

Or, $\boxed{n_1 = n_0}$ ... (1)

For $\frac{n_2}{n_1} = e^{\frac{\left[2.76\times10^{-21}-1.38\times10^{-21}\right]}{1.38\times10^{-23}\times100K}}$

$$\frac{n_2}{n_1} = e^{-1} \text{ or } \frac{n_2}{n_1} = \frac{1}{e} \text{ or } n_1 = en_2 \qquad \text{... (2)}$$

From equation (1) and (2)

$$n_0 = n_1 = n_2 e$$

$$\therefore \quad \bar{E} = \frac{n_0E_0 + n_1E_1 + n_2E_2}{n_0 + n_1 + n_2}$$

Or, $\left(n_0 + n_1 + n_2\right)\bar{E} = n_0E_0 + n_1E_1 + n_2E_2$

Or, $\left(n_0 + n_1 + n_2\right)\bar{E} = n_0E_0 + n_0E_1 + \frac{n_0}{e}E_2 \qquad \left[\because \left(n_0 + n_1 + n_2\right)\bar{E} = 1.38\times10^{-18}J\right]$

Or, $1.38\times10^{-18}J = n_0\left[1.38\times10^{-21} + 1.38\times10^{-21} + 2.76\times10^{-21}\right]$

Or, $1.38\times10^{-18}J = n_0\times\left[2.76\times10^{-21} + 1.01\times10^{-21}\right]$

Or, $1.38\times10^{-18}J = n_0 3.77\times10^{-21}$

$$n_0 = 0.366\times10^3$$

$$n_0 = 366$$

From equation (1), we get

Or, $$\Sigma n = 366 + 366 + \frac{366}{2.71} = 867 \approx 1000 \text{ (approximate)}$$

16. The molecular partition function for a system in which the energy levels are equispaced by ε, is

(a) $\frac{1}{1+e^{\beta\varepsilon}}$ (b) $\frac{1}{1-e^{\beta\varepsilon}}$ (c) $\frac{1}{1+e^{-\beta\varepsilon}}$ (d) $\frac{1}{1-e^{-\beta\varepsilon}}$ **[GATE 2014]**

Soln. The molecular partition function, if energy level of a system are equispaced by ε, is gives as

Molecular partition function $= \frac{1}{1-e^{-\beta\varepsilon}}$ where, $\beta = \frac{1}{kT}$

Correct option is (d)

17. The temperature dependence of partition functions are as follows: **[GATE 2013]**

$q_{translational} \propto T^{3/2}$ $q_{vibration} \propto T^{0}$

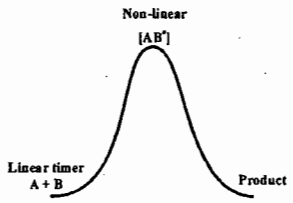
$q_{rotation} \propto T$ (linear molecule) $q_{rotation} \propto T^{3/2}$ (non-linear molecule)

According to the conventional transition state theory (CTST), the temperature dependence factor for a reaction of the type given below is

Linear molecule + linear molecule $\rightleftharpoons$ non-linear transition state $\rightarrow$ products

(a) T^{-1} (b) T^{0} (c) T^{1} (d) T^{2}

Soln. $A + B \longrightarrow AB^{\#} \longrightarrow$ Product



$$k_p = \left(\frac{RT}{P}\right)^{\Delta n_g}\left[\frac{q_{AB^{\#}}}{q_A\, q_B}\right] = \left(\frac{RT}{P}\right)^{-1}\left[\frac{T^{3/2}\cdot T}{T^{3/2}\cdot T}\right] \propto T^{-1}$$

Rate $= AB^{\#} = k_P[A][B]$.

$AB^{\#} = Rate \longrightarrow frequency$

$$A = \frac{1}{T},\ A \propto T^{-1}$$

Correct option is (a)

18. The molecular partition function of a system is given by **[GATE 2012]**

$$q(T) = \left(\frac{k_B T}{hc}\right)^{3/2}\left(\frac{8\pi^3 m k_B T}{h^2}\right)^{3/2}$$, where the symbols have their usual meanings.

The heat capacity at constant volume for this system is

(a) $3R$ (b) $6R$ (c) $9R/2$ (d) $3R/2$

Soln. Given : $q(T)=\left(\frac{k_BT}{hc}\right)^{3/2}\left(\frac{8\pi^2mk_BT}{h^2}\right)^{3/2}$

$$\Rightarrow \quad q(T)=\left(\frac{8\pi^2mk_B^2}{h^3}\right)^{3/2}\times T^3$$

$$\Rightarrow \quad \ell nq(T)=\ell n\left[\left(\frac{8\pi^2mk_B^2}{h^3}\right)^{3/2}\right]+\ell nT^3$$

For 1 mole of the system internal energy is given by

$$U=RT^2\left(\frac{\partial \ell nq}{\partial T}\right)_V=RT^2\times\frac{3}{T}=3RT$$

The molar heat capacity at contant volume (C_v) is given by

$$C_V=\left(\frac{\partial U}{\partial T}\right)_V=3R$$

Correct option is (a)

19. For an ideal gas with molar mass *M*, the molar translational entropy at a given temperature is proportional to
(a) $M^{3/2}$ (b) $M^{1/2}$ (c) e^M (d) ln(M) **[GATE 2015]**

Soln. Since, we know that

$$S=k\ln W$$

For molar mass *M*, the molar translational entropy is

$$S_m=k\ln M \quad \text{Or,} \quad S_m\propto \ln M$$

Correct option is (d)

20. The vibrational partition function for a molecule which can be described as a simple harmonic oscillator with fundamental frequency υ is given by **[GATE 2005]**

(a) $\exp\left(-\frac{h\nu}{k_BT}\right)$ (b) $\left[1-\exp\left(-\frac{h\nu}{k_BT}\right)\right]^{-1}$

(c) $\exp\left(-\frac{h\nu}{k_BT}\right)\left[1-\exp\left(-\frac{h\nu}{k_BT}\right)\right]^{-1}$ (d) $\exp\left(-\frac{h\nu}{2k_BT}\right)\left[1-\exp\left(-\frac{h\nu}{k_BT}\right)\right]^{-1}$

Soln. For harmonic oscillator, its vibrational energy is

$$\varepsilon_v=\left(v+\frac{1}{2}\right)h\nu_0;\quad v=0,1,2,.....$$

where, ν_0, the classical frequency of oscillation

Since, the vibrational energy levels are non-degenerate, the expression of vibrational partition function is given by

$$q_v=\sum_{v=0}^{\infty}\exp\left(-\frac{h\nu_0\left(v+\frac{1}{2}\right)}{kT}\right)$$

$$q = e^{-\frac{h\nu_0}{2kT}} + e^{-\frac{3h\nu_0}{2kT}} + e^{-\frac{5h\nu_0}{2kT}} + \ldots\ldots$$

$$= \frac{e^{-\frac{h\nu_0}{2kT}}}{1 - e^{-\frac{h\nu_0}{kT}}} = \exp\left(-\frac{h\nu}{2k_BT}\right)\left[1 - \exp\left(-\frac{h\nu}{k_BT}\right)\right]^{-1}$$

where,

$$\boxed{q = \frac{1}{2\sinh\left(\frac{h\nu_0}{2kT}\right)}}$$

Correct option is (d)

21. Rotational partition function for H_2 molecule

Soln. H_2 is a half integer (spin i = ½).

Rotational partition function for such molecule

$$Z_{rot} = \left(Z'_{even}\, Z_{even} + Z'_{odd}\, Z_{odd}\right) \quad \ldots (i)$$

Calculate

$$Z'_{even} = \frac{i}{2i+1} = \frac{½}{2\times\frac{1}{2}+1} = \frac{1}{4}$$

$$Z'_{odd} = \frac{i+1}{2i+1} = \frac{½+1}{2\times\frac{1}{2}+1} = \frac{3}{4}$$

$$Z_{even} = \sum_{J=0,2,4} (2J+1)\, e^{-\beta BhcJ(J+1)}$$

$$Z_{odd} = \sum_{J=1,3,5} (2J+1)\, e^{-\beta BhcJ(J+1)}$$

Put the vlaue in equation first

$$Z_{rot} = \frac{1}{4}\sum_{J=0,2,4} (2J+1)\, e^{-\beta BhcJ(J+1)} + \frac{3}{4}\sum_{J=1,3,5} (2J+1)\, e^{-\beta BhcJ(J+1)}$$

$$Z_{rot} = \frac{1}{4}\left[\sum_{J=0,2,4} (2J+1)\, e^{-\beta BhcJ(J+1)} + 3\sum_{J=1,3,5} (2J+1)\, e^{-\beta BhcJ(J+1)}\right]$$

22. Calculate the rotational partition function for D_2 molecule.

D_2 is spin one integer (i = 1) rotational partition function for such molecule

$$Z_{rot} = \left(Z'_{even}\, Z_{even} + Z'_{odd}\, Z_{odd}\right) \quad \ldots (i)$$

Calculate

$$Z'_{even} = \frac{i+1}{2i+1} = \frac{1+1}{2+1} = \frac{2}{3}$$

$$Z'_{odd} = \frac{i}{2i+1} = \frac{1}{3}$$

$$Z_{even} = \sum_{J=0,\,2,\,4\ldots} (2J+1) e^{-\beta BhcJ(J+1)} \qquad [\text{Where, } \beta = \frac{1}{k_B T}]$$

$$Z_{odd} = \sum_{J=1,\,3,\,4\ldots} (2J+1) e^{-\beta BhcJ(J+1)}$$

Put the value in equation (i)

$$Z_{rot} = \left(Z'_{even}\, Z_{even} + Z'_{odd}\, Z_{odd}\right)$$

$$= \frac{2}{3} \sum_{J=0,2,4,\ldots} (2J+1)\, e^{-\beta BhcJ(J+1)} + \frac{1}{3} \sum_{J=1,3,5} (2J+1)\, e^{-\beta BhcJ(J+1)}$$

$$= \frac{1}{3}\left[2 \sum_{J=0,2,4,\ldots} (2J+1)\, e^{-\beta BhcJ(J+1)} + \sum_{J=1,3,5} (2J+1)\, e^{-\beta BhcJ(J+1)} \right]$$

23. The rotational partition function of H_2 is: **[NET Dec. 2012]**

(a) $\sum_{J=0,\,1,\,2\ldots..} (2J+1)\, e^{-\beta hcBJ(J+1)}$

(b) $\sum_{J=1,3,\,5,\ldots..} (2J+1)\, e^{-\beta hcBJ(J+1)}$

(c) $\sum_{J=0,2,4\ldots..} (2J+1)\, e^{-\beta hcBJ(J+1)}$

(d) $\frac{1}{4}\left[\sum_{J=0,2,4\ldots..} (2J+1)\, e^{-\beta hcBJ(J+1)} + 3 \sum_{J=1,3,5\ldots..} (2J+1)\, e^{-\beta hcBJ(J+1)} \right]$

PRACTICE SET

1. Which of the following is true

(a) $q_{tr} > q_{vib} > q_{el} > q_{rot}$ (b) $q_{tr} > q_{rot} > q_{vib} > q_{el}$

(c) $q_{tr} >> q_{rot} >> q_{vib} >> q_{el}$ (d) $q_{el} > q_{vib} > q_{rot} > q_{tr}$

2. In terms of the molar partition function q, the internal energy of a molecule is given by

(a) $U = nRT^2 \left(\partial \ell nq / \partial V\right)_T$ (b) $U = nRT\left(\partial \ell nq / \partial V\right)_T$

(c) $U = nRT^2 \left(\partial \ell nq / \partial T\right)_V$ (d) $U = nRT\left(\partial \ell nq / \partial T\right)_V$

3. A system has 100 degenerate energy levels and 100 bosons are kept in it. Find the entropy of the system equilibrium.

(a) $10^{-2}\ k_B$ (b) $10^2\ k_B$ (c) $460.6\ k_B$ (d) $4.606\ k_B$

4. Calculate the total number of microstates for 6 identical particles with their occupation numbers {1, 2, 3} three states is:

(a) 6 (b) 12 (c) 60 (d) 720

5. The energy levels of the harmonic oscillator (neglecting zero point energy) are $\varepsilon_v = nh\nu$ for $n = 0, 1, 2, ...$

Assuming $h\nu = k_B T$, the partition function is:

(a) e (b) $\frac{1}{e}$ (c) $1-\frac{1}{e}$ (d) $\frac{1}{1-\frac{1}{e}}$

6. A system consisting of 4 identical and distinguishable particle, each possessing three available states of 1, 2 and 3 units, has 10 units of energy. The number of ways, W, in which these conditions are satisfied is

(a) 2 (b) 4 (c) 6 (d) 10

7. The number of ways in which four molecules can be distributed in two different energy levels is

(a) 6 (b) 3 (c) 16 (d) 8

8. The translational partition function of a hydrogen molecule confined in a 100 mL flask at 298 K (Mol. wt. of hydrogen = 2.016) is:

(a) 2.8×10^{20} (b) 2.8×10^{25} (c) 2.8×10^{26} (d) 2.8×10^{27}.

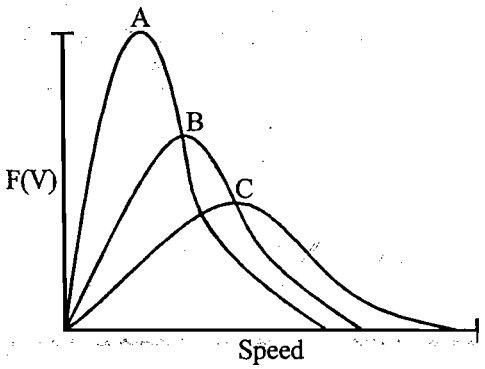
9. The translational, rotational and vibrational partition functions for a molecule are

$f_{translation} \simeq 10^{10}\ m^{-1}$, $f_{rotation} \simeq f_{vibration} \simeq 1$, $\left(k_B T / h\right) \simeq 10^{13}$ at room temperature, $N_A \simeq 6\times10^{23}$

Using the approximate data given above, the frequency factor (A) for a reaction of the type:
atom + diatomic molecule $\rightarrow$ non-linear transtion state $\rightarrow$ product, according to the conventional transition state theory is

(a) 2×10^3 (b) 6×10^7 (c) 2×10^{12} (d) 6×10^{13}

10. [CSIR DEC. 2014]



Identify the speed distribution functions of Ne, Ar, and Kr with the curves in the figure above

(a) Ne-A, Ar-B, Kr-C (b) Ne-B, Ar-C, Kr-A [CSIR DEC. 2014]

(c) Ne-C, Ar-B, Kr-A (d) Ne-C, Ar-A, Kr-B

11. The low and high temperature limits of vibrational partition function are $\left(\theta = \frac{h\nu}{k}\right)$ [CSIR DEC. 2014]

(a) $e^{-\theta/T}$ and $\frac{T}{\theta}e^{-\theta/T}$ (b) $e^{-\theta/2T}$ and $\frac{T}{\theta}e^{-\theta/2T}$

(c) $e^{-\theta/2T}$ and $\frac{T}{\theta}e^{-\theta/T}$ (d) $e^{-\theta/2T}$ and $\frac{\theta}{T}e^{-\theta/2T}$

12. The probability of finding the harmonic oscillator in the energy level $n = 1$ is (neglect zero point energy and assume $h\nu = k_B T$) [CSIR DEC : 2014]

(a) e (b) e^2 (c) $1 - e^{-2}$ (d) $e^{-2}(e-1)$

13. If θ_r denotes the characteristic tempreture of rotation then the magnitude of $\left[\theta_r(H_2)\theta_r(D_2)\right]/\left[\theta_r(HD)\right]^2$ (assume the bond lengths to be the same for all the molecules) is

(a) 2/3 (b) 3/2 (c) 8/9 (d) 9/8

14. The rotational partition function of a diatomic molecule with energy levels corresponding to J = 0, 1, is (where, ε is a constant) [GATE 2015]

(a) $1+2e^{-2\varepsilon}$ (b) $1+3e^{-2\varepsilon}$ (c) $1+e^{-3\varepsilon}$ (d) $1+3e^{-3\varepsilon}$

15. A molecule has a ground state and two excited electronic energy levels, all of which are nondegenerate with the energies: $E_0 = 0$, $E_1 = 1\times10^{-20}$ J, and $E_2 = 3\times10^{-20}$ J. If P_0, P_1 and P_3 are fractions of molecules occupied in ground, first and second excited states, respectively, at 298K, then, $P_0 : P_1 : P_2 = ?$

(a) 0.919 : 0.081 : 0.001 (b) 0.900 : 0.098 : 0.002

(c) 0.666 : 0.333 : 0.111 (d) 0.880 : 0.088 : 0.022

ANSWER KEY					
Questions	1	2	3	4	5
Option	(c)	(c)	(b)	(c)	(d)
Questions	6	7	8	9	10
Option	(d)	(c)	(c)	(b)	(c)
Questions	11	12	13	14	15
Option	(b)	(d)	(c)	(b)	(a)

Chapter 9

Kinetic Theory of Gases

Kinetic Theory of Gases:

Kinetic theory of gases which provided sound theoretical basis for the various gas laws, mainly Boyle's law, Charle's law, Graham's law and Avogadro's law. These laws were empirical generalization based on experimental observation. There was no theoretical background to justify them.

It is based on following postulates

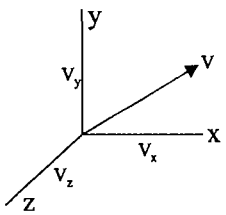
(i) Every gas consists of large number of tiny particles called gas molecules.
(ii) Gas molecules can move rapidly in every possible direction and colloid with one another and with walls of container.
(iii) Their collisions are perfectly elastic i.e. there is no loss of momentum and energy.
(iv) The volume occupied by the gas molecule is negligible as compared to the total volume of gas.
(v) There is no attraction or repulsion between gas molecules or gas and waals of vessel.
(vi) The pressure of the gas is due to bombardment of gas molecules on the waals of vessel.
(vii) Their is no effect of gravity on the distribution of gas in the container.
(viii) The average kinetic energy of gas molecule is directly proportional to the absolute temperature.

$$\boxed{K.E. \propto T}$$

Derivation of Kinetic gas equation :

Let us consider that gas is kept in a cubical box of length 'a' & move with velocity 'v'. The mass of one gas particle be 'm'. The resolution of velocity 'v' along x, y, z axes.

$$\therefore \quad \boxed{v^2 = V_x^2 + V_y^2 + V_z^2} \qquad \ldots (1)$$

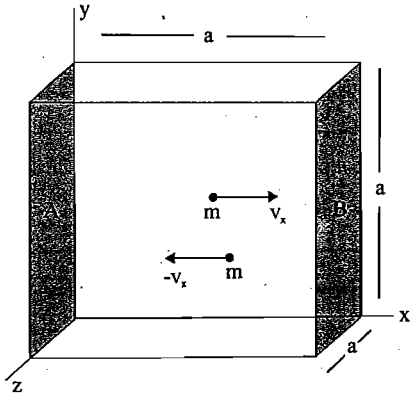


If a gas particle moves in a cubical box along +ve direction of x-axis with v_x velocity between two faces 'A' and 'B'.

momentum of the particle before collision to face 'B' = mv_x

momentum after collision = $-mv_x$.

Therefore, Change in momentum of particle = $-mv_x - mv_x = -2mv_x$



Therefore, Momentum transferred to the face B, $\Delta p = 2mv_x$

On colliding with the same face 'B' the molecule travel 2a distance with v_x velocity

$\therefore \quad \Delta t = \dfrac{2a}{v_x}$

$\therefore$ Change in momentum per unit time at B face,

$$\frac{\Delta p}{\Delta t} = \frac{2mv_x}{2a}.v_x = \frac{mv_x^2}{a}$$

Change in momentum between A and B faces

$$= 2\left(\frac{mv_x^2}{a}\right)$$

According to Newton's law,

Change in momentum per unit time = Force

$\therefore \quad F = \dfrac{2mv_x^2}{a}$

Similarly, along y and z axes $\dfrac{\Delta p}{\Delta t}$ are $\dfrac{2mv_y^2}{a}$ and $\dfrac{2mv_z^2}{a}$ respectively.

$\therefore$ Total change in momentum $= \dfrac{2mv_x^2}{a} + \dfrac{2mv_y^2}{a} + \dfrac{2mv_z^2}{a} = \dfrac{2m}{a}\left(v_x^2 + v_y^2 + v_z^2\right)$

$$\boxed{F = \frac{2mv^2}{a}} \quad \left(\text{from equation(1), } v^2 = v_x^2 + v_y^2 + v_z^2\right)$$

Area of cube $= 6\times(a)^2$

$\therefore \quad$ Pressure, $P = \dfrac{F}{A} \quad \Rightarrow \quad \dfrac{2mv^2}{a.6\,a^2}$

$$P = \frac{1}{3}\frac{mv^2}{a^3} \qquad \left(\because a^3 = \text{volume of cube } v\right)$$

$$P = \frac{1}{3}\frac{mv^2}{V} \qquad \left[\bar{v}^2 = \text{Root mean square velocity}\right]$$

For 1 mole, $\boxed{PV = \dfrac{1}{3}mv^2}$

For 'n' mole, $\boxed{PV = \dfrac{1}{3}mn\bar{v}^2}$ ... (2)

Equation (2) is known as kinetic gas equation.

Kinetic Energy of one mole of gas :

From Kinetic gas equation.

$PV = \dfrac{1}{3}mn\,\bar{v}^2$ $\left(m.n = M \text{ total mass of gas}\right)$

$PV = \frac{1}{3}M\bar{v}^2$ (multiply and divide by 2 on R.H.S.)

$PV = \frac{2}{3}\left(\frac{1}{2}M\bar{v}^2\right) \Rightarrow PV = \frac{2}{3}KE \Rightarrow \left(KE = \frac{1}{2}m\bar{v}^2\right) \Rightarrow KE = \frac{3}{2}PV$

From ideal gas equation $PV = RT$ 'for 1 mole'

$\therefore$ $\boxed{KE = \frac{3}{2}RT}$ ... (3)

Where, R = universal gas constant.

$\boxed{KE \propto T}$

Thus kinetic energy for 1 mole of gas is directly proportional to the temperature

Kinetic energy for 1 molecule:

$\because$ Kinetic energy for 1 mole $= \frac{3}{2}RT$.

$\therefore$ KE for molecule $= \frac{3}{2}\left(T\frac{R}{N_A}\right)$ (N_A = Avogadro's number)

$\boxed{KE = \frac{3}{2}kT}$ k= Boltzmann constant $(1.38\times10^{-23}\ J/K)$ ... (4)

$\boxed{KE \propto T}$

Thus kinetic energy for one molecule also depends on temperature.

Deduction of various gas laws from kinetic gas equation:

(1) Boyle's law:

$\because$ $PV = \frac{1}{3}m.n\bar{v}^2 \Rightarrow PV = \frac{1}{3}m\bar{v}^2$ (m.n = M total mass of gas)

$PV = \frac{2}{3}KE$

From equation (3), $KE \propto T$

$PV = \frac{2}{3}T$

If temperature of gas kept constant

PV = constant

$PV = K \Rightarrow P = \frac{K}{V}$ Or $\boxed{P \propto \frac{1}{V}}$ This is Boyle's law.

(2) Charle's law:

$PV = \frac{1}{3}m.n\bar{v}^2 \Rightarrow PV = \frac{1}{3}m\bar{v}^2$ (m.n = M)

$PV = \frac{2}{3}\left(\frac{1}{2}M\bar{v}^2\right) \Rightarrow PV = \frac{2}{3}KE$

$\because$ $KE \propto T \Rightarrow PV = \frac{2}{3}T \Rightarrow \frac{V}{T} = \frac{2}{3}P$

At constant pressure

$$\frac{V}{T} = k \Rightarrow V = kT \Rightarrow \boxed{V \propto T}$$ i.e. Charle's law.

(3) Avogadro's law:

One mole of any substance contains the Avogadro constant (6.022×10^{23}) of molecules. It was Avogadro who discovered the law of nature for gases. This law is known as Avogadro's law, which states:

The volumes of the same number of moles of all gases measured at constant temperature and pressure are the same. That is, at the same temperature and pressure equal volumes of all gases contain equal number of moles or molecules.

Let us consider that two gases having masses m_1, m_2 and number of moles n_1 and n_2 are at the same temperature pressure and volumes.

$\therefore$ From kinetic gas equation

$$PV = \frac{1}{3} m_1 n_1 v_1^2 \quad \text{... (i)}$$

$$PV = \frac{1}{3} m_2 n_2 v_2^2 \quad \text{... (ii)}$$

On comparing equation (i) and (ii), we get

$$\therefore \quad \frac{1}{3} m_1 n_1 v_1^2 = \frac{1}{3} m_2 n_2 v_2^2$$

$$m_1 n_1 v_1^2 = m_2 n_2 v_2^2 \quad \text{... (iii)}$$

Since both gases are at the same temperature hence they will have same KE.

$$\text{i.e.} \quad \frac{1}{2} m_1 v_1^2 = \frac{1}{2} m_2 v_2^2 \quad \text{... (iv)}$$

On dividing equation (iii) by equation (iv)

$$\frac{m_1 n_1 v_1^2}{m_1 v_1^2} = \frac{m_2 n_2 v_2^2}{m_2 v_2^2}$$

$\Rightarrow$ $n_1 = n_2$, this is known as Avogadro's law.

(4) Graham's law of diffusion:

"The rate of diffusion of a gas is inversely proportional to the square root of its density at constant pressure."

From kinetic gas equation.

$$PV = \frac{1}{3} mnv^2 \qquad [m.n = M \text{ total mass of gas}]$$

$$PV = \frac{1}{3} Mv^2 \Rightarrow v^2 = \frac{3PV}{M} = \frac{3P}{\left(\frac{M}{V}\right)} \Rightarrow v^2 = \frac{3P}{d}$$ where, d = density of gas

$$\therefore \quad v = \sqrt{\frac{3P}{d}}$$

If P = constant.

$$v \propto \frac{1}{\sqrt{d}}$$

This equation is known as Graham's law.

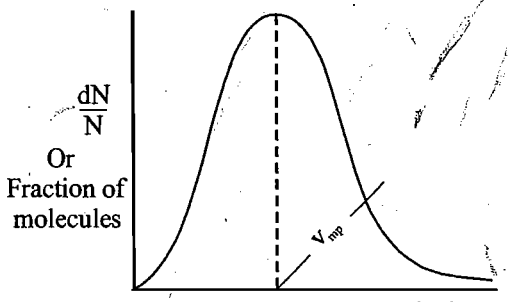
Maxwell's distribution of molecular velocities:

According to assumption of kinetic theory of gases, molecules of gas colloids with one another and with the walls of vessel, thus their velocities keep on changing which results in different speeds for different fraction of molecules at a gain temperature.

If N is the total number of molecules in a gas out of which ΔN molecules have the same speed, the fraction of molecules having same speed is given by $\frac{\Delta N}{N}$ or $\frac{dN}{N}$.

The quantity $\frac{dN}{N}$ gives the fraction of molecules with speeds between c and c+dc. It can also given by p(c)dc.

Maxwell plotted a graph between different values of the speeds and the corresponding molecular fractions which is known as 'Maxwell's distribution curve'.



$$\frac{dN}{N} = 4\pi\left(\frac{M}{2RT}\right)^{3/2} \exp\left(\frac{Mc^2}{2kT}\right) cdc$$

The important features of curve are given as:

(1) The fraction of molecules with too low or too high velocities are very small.

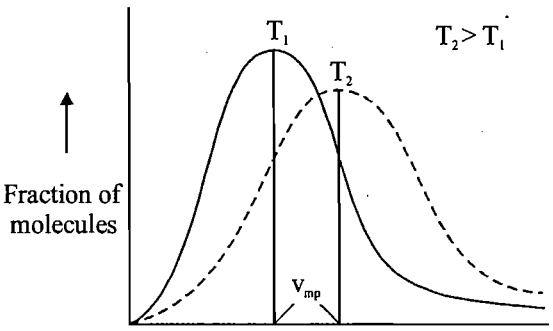
(2) The fraction of molecules possessing higher and higher speeds keeps on increasing till it reaches a certain maximum value and then starts decreasing as shown in the curve.

(3) There is a certain velocity for which the fraction of molecules is maximum. This is called the most probable velocity. Its value at a given temperature depends upon the volume of the gas.

Effect of temperature on distribution of molecular velocities:

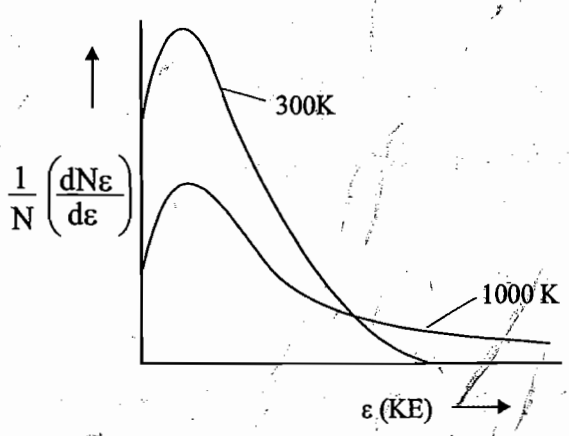
In molecular speeds at x-axes the factor $e^{-(mc^2/2kT)}$ called Boltzmann factor increases with the rise in temperature and thus molecular speeds increases. But the fraction of molecules having most probable velocity decreases with the rise in temperature.

Thus thickness of curye increases along with the decrease in height and curve shifts towards right with the rise of temperature



Maxwell's distribution of molecules kinetic energies:

It is a curve between the fraction of molecules having kinetic energies in the range of ε and $\varepsilon + d\varepsilon$ i.e. $\frac{dN\varepsilon}{N}$ versus kinetic energies ε.



The maximum in the probability function corresponds to the most probable kinetic energy.

Most probable kinetic energy

per mole $= \frac{1}{2}RT$

per molecule $= \frac{1}{2}kT$ [k = Boltzmann constant]

Types of Molecular velocities:

Molecular motions are of three types:

(1) Most probable speeds (v_{mp}):

The most probable speed is defined as the velocity possessed by maximum number of molecules of a gas at a given temperature. It is given by

$$v_{mp} = \sqrt{\frac{2RT}{M}} \quad \ldots (1)$$

M = molecular mass of gas.

(2) Average Speed (v_{av}):

It is the arithmatic mean of different velocities possessed by the molecules of the gas at a given temperature.

If $c_1, c_2, c_3 \ldots\ldots c_n$ are the individual velocities of the gas molecules and 'n' is their total number, then, average velocity is given by.

$$\langle v \rangle = \frac{c_1 + c_2 + c_3 \ldots\ldots c_n}{n} \quad \ldots (2)$$

If c_1, c_2, c_3 ..... are the velocities possessed by groups of n_1, n_2, n_3 ..... molecules of the gas respectively, average velocity is given by.

$$\langle c \rangle = \frac{n_1c_1 + n_2c_2 + n_3c_3 + \ldots\ldots}{n_1 + n_2 + n_3 + \ldots\ldots\ldots}$$

on solving Boltzmann - distribution of molecular velocities, average speed comes out to be

$$\langle v \rangle = \sqrt{\frac{8RT}{\pi M}} \quad \ldots (3)$$

(3) Root mean Square velocity:

It is the square root of the means of the squares of the speeds of the different molecules in a gas at a given temperature.

If c_1, c_2, c_3 ..... are the velocities possessed by groups of n_1, n_2, n_3 ..... molecules respectively.

$$\therefore \quad v_{rms} = \sqrt{\frac{n_1c_1^2 + n_2c_2^2 + n_3c_3^2 .....}{n_1 + n_2 + n_3 + ...}}$$

By solving Boltzmann equation v_{rms} is given by $v_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3PV}{M}}$ ... (4)

Relation between different types of Speeds:

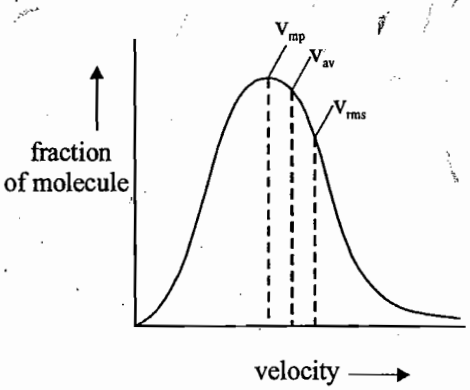
(i) Average speed = $0.9213 \times$ Root mean square speed

(ii) Most probable speed = $0.816 \times$ Root mean square speed.

$\therefore \; v_{rms} : v_{av} : v_{mp} = 1.224 : 1.128 : 1 = 1 : 0.92 : 0.82$

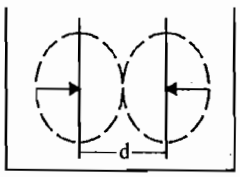
(iii) $v_{rms} > v_{av} > v_{mp}$

Thus, at a given temperature root mean square velocity of a gas is maximum and probable speed is minimum.



Collision diameter:

The distance between the centers of the two molecules at the point of their closest approach is known as collision diameter.



For two molecules to colloid they must have closer approach than collision diameter.

Collision number (z_1):

The number of collisions suffered by a single molecule per unit volume of the gas. It is given by

$$z_1 = \sqrt{2}\,\pi d^2 \langle v \rangle \rho \qquad \text{... (1)}$$

where, ρ = number of molecules per unit volume of the gas

$\langle v \rangle$ = Average velocity

d = collision diameter.

The total number of molecules colliding per unit time per unit volume of the gas

$$= \sqrt{2}\,\pi d^2 \langle v \rangle \rho^2 \qquad \text{... (2)}$$

Since each collisions involves two molecules, the number of collisions of like molecules per unit time per unit volume of gas is given by

$$z_{11} = \frac{1}{2}\sqrt{2}\,\pi d^2 \langle v \rangle \rho^2$$

$$\boxed{z_{11} = \frac{1}{\sqrt{2}}\pi d^2 \langle v \rangle \rho^2} \qquad \text{... (3)}$$

Collision frequency: The number of collisions experienced by molecules per cc of a gas per second is known as collision frequency.

$\because$ Total no. of molecules colliding per cc per sec. is $z = \sqrt{2}\,\pi\langle v\rangle N^2 d^2$

$\therefore$ Collision frequency $n = \frac{z}{2}$ [N = number of gas molecules]

$$\boxed{n = \frac{\pi\langle v\rangle d^2 N^2}{\sqrt{2}}} \quad \ldots(4)$$

Mean free path:

The mean free path is defined as the average distance travelled by a molecule between two successive collisions.

$$\lambda = \frac{\text{average distanace travelled per sec.}}{\text{number of collisions by a molecule per sec.}} = \frac{\langle v\rangle}{\sqrt{2}\pi\langle v\rangle d^2 N} \Rightarrow \lambda = \frac{1}{\sqrt{2}\pi d^2 N}$$

Assuming that the collision diameter, σ, is independent of temperature, the temperature and pressure dependence of the mean free path is given by ideal gas law as

$$\lambda = \frac{\langle V\rangle}{z_1} \Rightarrow \boxed{\lambda = \frac{kT}{\sqrt{2}\pi d^2 . p}} \quad \ldots(5)$$

$\therefore$ $\lambda \propto \frac{1}{p}$ at constant 'T'

$\lambda \propto T$ at constant. 'p'

Degree of freedom:

The degrees of freedom of a molecule are defined as the independent number of parameters required to describe the state of the molecule completely. Each molecule has 3N degree of freedom. Where N is total number of atoms in 1 mole of molecular formula.

It is of three types:

(i) **Translational degree of freedom:**

Each molecule has three translational degree of freedom along three axes x, y and z.

Monoatomic gases, He, Ne, Ar etc. posses only 3 translational degree of freedom. They have no rotational or vibrational degree of freedom.

(ii) **Rotational degrees of freedom:**

- All linear molecule, such as CO_2, C_2H_2, HCl has 2 rotational degrees of freedom.
- Non-linear molecule, such as H_2O, NH_3, CH_4, H_2S etc.has 3 rotational degrees of freedom.

(iii) **Vibrational degree's of freedom:**

- for linear molecule (CO_2, C_2H_2) = 3N – 5
- for non-linear molecule (H_2O, NH_3, CH_4) = 3N–6

Note:

(i) Rotational degrees of freedom present only in liquid and gases.

(ii) In solid state molecule possess only vibrational degrees of freedom.. Translational and rotational motion in solids converted into vibrational motion.

Principle of Equipartition of Energy:

According to the law of equipartition of energy, the total energy of a molecule is divided equally amongst the various degrees of freedom of molecule.

Since average kinetic energy of a molecule $= \frac{3}{2}kT$

Therefore according to equipartition principle, energy divided to each degree of freedom

$$= \frac{1}{3} \times \frac{3}{2}kT = \frac{1}{2}kT \text{ or } \frac{1}{2}RT \text{ per mole.}$$

Thus kinetic energy for each degrees of freedom is $\frac{1}{2}kT$ per molecule or $\frac{1}{2}RT$ per molecule.

In vibrational motion two atoms oscillate against each other, and possess both potential & kinetic energy. Thus energy of vibration involves two degrees of freedom.

$\therefore$ Energy of vibration per molecule $= 2 \times \frac{1}{2}kT = kT$ or RT per mole.

Therefore, (i) Energy of translation for each degree of freedom $= \frac{1}{2}kT = \frac{1}{2}RT$

(ii) Energy of rotation for each degree of freedom $= \frac{1}{2}kT = \frac{1}{2}RT$

(iii) Energy of vibration for each degree of freedom $= kT = RT$

Thus, if n_1, n_2 and n_3 are the translational, rotational and vibrational degrees of freedom, the total energy

$$\boxed{= n_1 . \frac{1}{2}kT + n_2 . \frac{1}{2}kT + n_3 kT}$$

Root mean square velocity from kinetic gas equation :

From kinetic gas equation,

$$PV = \frac{1}{3}mn\bar{v}^2 \qquad \ldots (1)$$

Where, p = Pressure of gas, v = volume of gas, m = mass of 1 gas molecule
n = number of moles of gas, $\bar{v}$ = Root mean square velocity.

$$PV = \frac{1}{3}M\bar{v}^2 ; \text{ (m.n = M total mass of gas/mol. mass)}$$

$$3PV = M\bar{v}^2 ; \quad \Rightarrow \bar{v}^2 = \frac{3PV}{M}$$

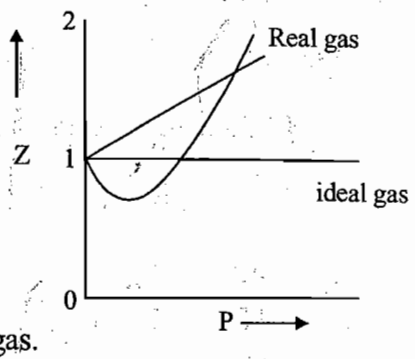
$$\boxed{V_{rms} = \sqrt{\frac{3PV}{M}}} \text{ or } \boxed{V_{rms} = \sqrt{\frac{3RT}{M}}} \quad [\because PV = RT]$$

Real gases: Van der Waals equation:

To display the deviation of a gas from ideal behaviour clearly, the ratio of the observed molar volume, v, to the ideal molar volume $\left(V_{id} = \frac{RT}{P}\right)$ is plotted against pressure at constant temperature. This ratio is called the compressibility factor, Z,

$$Z = \frac{V_{real}}{V_{ideal}} = \frac{V_{real}p}{RT}$$

$$\left[V_{ideal} = \frac{RT}{P}\right]$$



For an ideal gas = $Z = 1$, For a real gas $z \neq 1$

(i) If $Z > 1$, the gas is less compressible compared to an ideal gas.
(ii) If $Z < 1$, the gas is more compressible compared to an ideal gas.
The gas which do not obey ideal gas laws is known as real gas.

A gas under low P and high T obey ideal gas equation but at low temperature and high pressure it deviates from ideal gas laws.

Van der Waal modified ideal gas equation PV= nRT to make it applicable for real gas at all temperature and pressure, which is as

$$\left(P + \frac{n^2a}{v^2}\right)(v - nb) = nRT \text{ for 'n' mole.}$$

Where $\frac{n^2a}{v^2}$ = pressure correction factor and measure of intermolecular force of attraction.

nb = volume correction and called excluded volume.

Unit of a = atm. lit^2 $mole^{-2}$ and b = lit. $mole^{-1}$

where, 'b' is four times the actual volume of gaseous molecules.

$$\boxed{b = 4 \times \text{Avogadro constant} \times \frac{4}{3}\pi r^3}$$

where, r = radius of gas molecules.

Boyle's Temperature (T_b):

The temperature of a gas at which it behaves ideally even at high pressure, is called 'Boyle temperature'(T_b).

$$\boxed{T_b = \frac{a}{Rb}}$$

SOLVED PROBLEMS

1. Estimate C_V (molar heat capacity at constant volume) for
(i) HCl (ii) He (iii) CO_2 (iv) NH_3 (v) CH_4

Soln. (i) HCl - linear diatomic molecule.

Translational degree of freedom = 3, $E_T = \frac{3}{2}RT$

Rotational degree of freedom = 2(linear), $\therefore E_R = 2 \times \frac{1}{2}RT = RT$

Vibrational degree of freedom = $3 \times 2 - 5 = 1$; $E_v = RT$

$\therefore$ Total energy = $\frac{3}{2}RT + RT + RT \Rightarrow U = \frac{7}{2}RT$

$$\therefore \left(\frac{dU}{dT}\right)_V = \frac{7}{2}R\left(\frac{dT}{dT}\right)_V \Rightarrow \boxed{C_V = \frac{7}{2}R}$$

(ii) **For He :**

Only 3 translational degree of freedom

$\therefore \quad U = 3\times\frac{1}{2}RT = \frac{3}{2}RT$

$\therefore \quad \left(\frac{dU}{dT}\right)_v = \frac{3}{2}R\left(\frac{dT}{dT}\right)_v \quad \Rightarrow \boxed{C_V = \frac{3}{2}R}$

(iii) **For CO_2 - linear:**

Translational degree of freedom = 3 $\quad \therefore \quad E_T = \frac{3}{2}RT$

Rotational degree of freedom = 2 $\quad \therefore \quad E_R = RT$

Vibrational degree of freedom = $3\times3-5$, $E_V = 4RT = 4$

$\therefore$ Total energy (U) = $4RT + RT + \frac{3}{2}RT = \frac{13}{2}RT$

$\therefore \quad C_V = \frac{13}{2}R\left(\frac{dT}{dT}\right)_V \quad \Rightarrow \boxed{C_V = \frac{13}{2}R}$

(iv) **NH_3 - Bent:**

Translational degree of freedom = 3; $E_T = \frac{3}{2}RT$

Rotational degree of freedom= 3; $E_R = \frac{3}{2}RT$

Vibrational degree of freedom = $3\times4-6=6$; $E_v = 6RT$

$\therefore$ Total energy $(U) = \frac{3}{2}RT + \frac{3}{2}RT + 6RT = 9RT$

$\therefore \quad \left(\frac{dU}{dT}\right)_V = \left(\frac{d}{dT}9RT\right)_V \Rightarrow \boxed{C_v = 9R}$

(v) **For CH_4:**

Non - linear molecule.

Translational degree of freedom = 3 ; $E_T = \frac{3}{2}RT$

Rotational degree of freedom = 3 ; $E_R = \frac{3}{2}RT$

Vibrational degree of freedom = $3\times5-6=9$ $\quad E_v = 9RT$

$\therefore \quad U = \frac{3}{2}RT + \frac{3}{2}RT + 9RT$

$U = 12RT$

$\therefore \quad \left(\frac{dU}{dT}\right)_V = \left(\frac{d}{dT}12RT\right)_V \quad \Rightarrow \boxed{C_v = 12R}$

Note: At room tempeature the contribution of vibrational energy towards total energy is 20% (or 0.20) for each vibrational degree of freedom

2. Find $\gamma\left(\frac{C_P}{C_V}\right)$ for (i) He and (ii) CH_4 at room temp.

Soln. (i) He only Translational degree of freedom = 3

$$U = E_T = \frac{3}{2}RT \quad \Rightarrow C_V = \frac{3}{2}R$$

$$\Rightarrow C_P = C_V + R = \frac{3}{2}R + R = \frac{5}{2}R$$

$$\therefore \quad \gamma = \frac{C_P}{C_V} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = 1.66$$

(ii) **CH_4:**

Translational degree of freedom = 3; $E_T = \frac{3}{2}RT$

Rotational degree of freedom = 3 ; $E_R = \frac{3}{2}RT$

Vibrational degree of freedom $= 3\times5-6=9$; $\therefore \quad E_V = 0.20\times9RT = 1.8RT$

$$\therefore \quad \text{Total energy} = \frac{3}{2}RT + \frac{3}{2}RT + 1.8RT$$

$$U = 4.8RT, \quad C_V = 4.8R$$

$$C_P = 4.8R + R = 5.8R, \ \gamma = \frac{C_P}{C_V} = \frac{5.8R}{4.8R} = 1.2$$

3. Calculate the temperature at which the average velocity of oxygen equals that of hydrogen at 20 K.

Soln. $\langle v\rangle = \sqrt{\frac{3RT}{M}}$

$$\Rightarrow \langle v\rangle \propto \sqrt{\frac{T}{M}}; \ [M = \text{mol. mass of gas}]$$

$$\therefore \quad \frac{\langle v\rangle \text{ oxygen}}{\langle v\rangle \text{ hydrogen}} = \sqrt{\frac{T_{O_2}}{M_{O_2}} \times \frac{M_{H_2}}{T_{H_2}}} = \sqrt{\frac{T_{O_2}\times2}{32\times20}}$$

Given that $T_{H_2} = 20K$, $M_{H_2} = 2$ and $M_{O_2} = 32$

$$1 = \sqrt{\frac{T_{O_2}}{320}} \qquad \left[\because \langle v\rangle_{O_2} = \langle v\rangle_{H_2}\right]$$

$$[1]^2 = \left[\left(\frac{T_{O_2}}{320}\right)^{1/2}\right]^2 \Rightarrow 1 = \frac{T_{O_2}}{320} \Rightarrow \boxed{T_{O_2} = 320K}$$

4. Calculate the root mean square velocity of nitrogen at 27°C and 70 cm pressure. Density of Hg = 13.6 g

Soln. $P_1 = 70$ cm $\quad P_2 = 76$ cm

$V_1 = ?$ $\quad V_2 = .0224\ cm^3$ } at STP

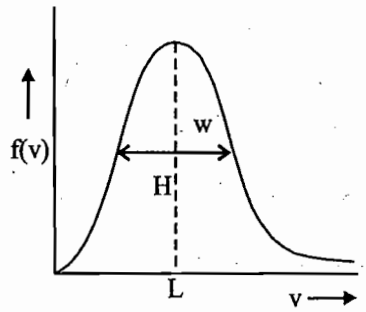
$T_1 = 300$ K ; $T_2 = 273$ K

$$\therefore \quad \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \Rightarrow V_1 = \frac{P_2V_2T_1}{P_1T_2} = \frac{76\times.0224\ m^3\times300}{70\times273} \Rightarrow V_1 = 0026725\ m^3$$

$$\text{Pressure in MKS unit (P)} = \frac{70}{76}\times101325\ Nm^{-2}$$

$$v_{rms} = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3\times(70/76)\times101325\times0.026725\ m^3\ mole^{-2}}{28\times10^{-3}\ kg.mole^{-1}}} = 517\ ms^{-1}$$

5. The maxwell Boltzmann distribution for molecular speeds is shown in the following figure. In the figure, H is the height of the Peak, L is the location at the maxima and W is the width at half height. As the temperature is decreased.



(a) H increases, L decreases and W increases. (b) H increases, L decreases and W decreases.

(c) H decreases, L decreases and W increases (d) H decreases, L decreases and W decreases.

Soln. Correct answer is (b)

6. For the distribution of molecules velocities of gases, identify the correct order from following.

(a) $v_{rms} > v_{av} > v_{mp}$ (b) $v_{mp} > v_{rms} > v_{av}$ (c) $v_{av} > v_{rms} > v_{mp}$ (d) $v_{mp} > v_{av} > v_{rms}$

Soln. Correct answer is (a)

7. Justify the considering CO_2 as an ideal gas, equipartition theorem predicts its total energy as 6.5 KT.

Soln. CO_2 is linear molecule.

Translation DOF = 3; Rotational DOF = 2; Vibrational DOF $= 3\times3-5=4$

$$\text{Total energy} = \frac{3}{2}RT + RT + 4RT = 6.5RT \text{ per mole}$$

For 1 molecule:

$$E_{Total} = 6.5\left(\frac{TR}{N_A}\right) = 6.5kT \quad [\text{where } k = \frac{R}{N_A}, N_A \text{ is a Avogadro number}]$$

PRACTICE SET

1. If the temperature of a gas is doubled, the rms speed of molecules.
(a) increases by a factor of 2. (b) decreases by a factor of 2.
(c) increases by a factor of $\sqrt{2}$ (d) decreases by a factor of $\sqrt{2}$.

2. The ratio of the temperatures at which the average velocity of ethane (T_1) is equal to the root mean square velocity of benzene (T_2) is:
(a) 0.151 (b) 0.48 (c) 1.209 (d) 0.389

3. Given that the mean speed of H_2 is 1.78 km s^{-1}, the mean speed of D_2 will be
(a) 1.26 km s^{-1} (b) 2.52 km s^{-1} (c) 5.04 km s^{-1} (d) 3.17 km s^{-1}.

4. The v_{rms} of a gas at 300 K is 30 $R^{½}$. The molar mass of the gas, in kg mol^{-1}, is
(a) 1.0 (b) 1.0×10^{-1} (c) 1.0×10^{-2} (d) 1.0×10^{-3}

5. The molecular weight of an ideal gas having a density of 1.5 gL^{-1} at 100°C and 600 Torr is
(a) 45.9 g/mol (b) 4.59 g/mol (c) 5.82 g/mol (d) 58.2 g/mol

6. The virial expansion for a real gas can be written in either of the following forms:

$$\frac{P\bar{V}}{RT} = 1 + B_P P + C_P P^2 + ...$$

$$= 1 + B_V V + C_v V^2 + ...$$

If $B_V = \alpha B_P$, the value of α would be
(a) PV/RT (b) RT/PV (c) PV (d) RT

7. For an assembly of molecules (molar mass = M) at temperature T, the standard deviation of Maxweller's speed is approximately

(a) $0.7\sqrt{\frac{RT}{M}}$ (b) $1.4\sqrt{\frac{RT}{M}}$ (c) $0.7\sqrt{\frac{M}{RT}}$ (d) $1.4\sqrt{\frac{M}{RT}}$

8. The temperature of a sample of a gas is raised from 127°C to 527°C. The average kinetic energy of the gas.
(a) does not change (b) is doubled (c) is halved (d) cannot be calculated.

9. The kinetic energy of N molecules of O_2 is x Joules at –123°C. Another sample of O_2 at 27°C has kinetic energy of 2x Joules. The latter sample contains.
(a) N molecules of O_2 (b) 2N molecules of O_2
(c) $\frac{N}{2}$ molecules of O_2 (d) None of these.

10. The kinetic energy of any gas molecules at 0°C is.
(a) 5.66×10^{-21} J (b) 3408 J (c) 2 cal (d) 0

11. The ratio between the v_{rms} velocity of H_2 at 50K & that of O_2 at 800K is
(a) 4 (b) 1 (c) 1 (d) 1/4

12. The V_{rms} speed of N_2 molecules in a gas sample can be changed by -
(a) An increase in volume of sample (b) Mixing with Ar sample
(c) An increase in pressure on the gas (d) an increase in temperature

13. Among the following statements about the average velocity, $\langle v^0 \rangle$ of a gaseous molecule the one that is NOT true according to kinetic theory of gases is :

(a) $\langle v^0 \rangle$ increases as the square root of temperature increases
(b) $\langle v^0 \rangle$ decreases as the square root of mass decreases.
(c) $\langle v^0 \rangle$ increases as pressure decreases.
(d) $\langle v^0 \rangle$ does not change with the volume of container at a given temperature.

14. The rms velocity of N_2 molecules in a gas at a given temperature is 500 m/sec. The rms velocity of He at that temperature is (rounded to the nearest m/sec).

(a) 1750 m/sec (b) 1322 m/sec (c) 6125 m/sec (d) 661 m/sec

15. Given that the rms velocity of N_2 molecules in a gas is 500 m/sec at 27°C, the rms value at 320°C is
(a) 1000 m/sec (b) 2000 m/sec (c) 707 m/sec (d) 1740 m/sec

ANSWER KEY					
Questions	1	2	3	4	5
Option	(c)	(b)	(b)	(d)	(d)
Questions	6	7	8	9	10
Option	(d)	(a)	(b)	(a)	(a)
Questions	11	12	13	14	15
Option	(c)	(d)	(b)	(b)	(c)

Chapter 10

Chemical Equilibria

Introduction:

In a chemical reaction, chemical equilibrium is the state in which both reactant and products are present in concentration which have no further tendency to change with time. Usually this state result, when the forward reactant proceeds at the same rate as the reverse reaction. The reaction rates of the forward and backward reactions are generally not zero but equal. Thus, there are not net change in the concentration of reactant and products.

Le-Chatelier's Principle:

In order to predict qualitatively, the effect of variation in pressure or temperature on a system in equilibrium, we use Le Chatelier's principle.

The principle states, that, "Whenever stress is placed on any system in a state of equilibrium, then the system will always react in a direction which will tend to counteract the applied stress".

(a) Effect of pressure or Volume change on equilibrium:

The general rule of thumb:

"When the pressure is increased (i.e. volume is decreased without any addition or removal of gas to form the system) then composition of a gas phase equilibrium adjusts so as to reduce the number of molecules in the gas phase."

e.g. $N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)$

Condition (i):

If the above reaction is at equilibrium and suddenly pressure is increased, then it will move in forward direction, so that it will reduce the number of gaseous molecules.

Condition (ii):

If pressure is decreased, then reaction will move in backward direction such that, it will increase the overall number of molecules in gas

e.g. $H_2(g)+I_2(g) \rightleftharpoons 2HI(g)$

Here number of gaseous molecules on reactant side is same as number of gaseous molecules on product side, So this reaction is no way (by either going forward or backward) can reduce or increase number of molecules. So, above reaction will have no effect of change in pressure.

Problem-1. If the volume of the container in which the reaction $H_2(g)+I_2(s) \rightleftharpoons 2HI(g)$, is at equilibrium, is suddenly increased, so predict the direction of net reaction thereafter.

Soln. As volume has been increased, this implies that pressure has been decreased, so reaction will move in forward direction so that it can increase its number gaseous molecules.

Note: Pressure or Volume change affects the equilibrium only when there is difference in number of moles of gaseous molecules on the reactant side and product side. The number of moles of solid or liquid reactant and product are not counted.

(b) Effect of temperature:

When the reaction is endothermic, i.e., absorbs heat, addition of heat will favour it and reaction should proceed to a greater extent at higher temperature

The opposite is observed, if the reaction is exothermic.

e.g. $N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H^0 = -92\ kJ$

As the forward reaction is exothermic, so increase of temperature will led to reaction in backward direction i.e. dissociation of more NH_3 molecules.

e.g. $N_2(g)+O_2(g) \rightleftharpoons 2NO(g), \quad \Delta H^0 = +180\ kJ$

As the forward reaction is endothermic so higher temperature will favour the formation of NO molecules.

(c) Effect of addition of inert gas to the equilibrium reaction mixture:

Case I: Addition of inert gas at constant pressure has the same effect of decrease in pressure of gaseous molecules at equilibrium.

e.g. $N_2 + 3H_2(g) \rightleftharpoons 2NH_3(g)$

If inert gas 'Ar' is added to above reaction at equilibrium, then it has same effect as decreasing the pressure of system only.

Reaction will move in backward direction.

Case II: Addition of inert gas at constant volume has no effect on equilibrium.

Problem-2. For the equation reaction:

$Na_2HPO_4.2H_2O(s) \rightleftharpoons Na_2HPO_4(s)+2H_2O(g); \quad \Delta H^0 = +ve$

Predict the favorable condition for the decomposition of above dihydrate salt in terms of pressure change, temperature change and inert gas addition (if required).

Soln. (i) Pressure should be decreased.

(ii) Temperature should be increased

(iii) Inert gas should be added.

Mathematical chemistry of reaction which proceed at equilibrium by using free energy concept of thermodynamics. We use Gibbs Helmholtz equation and concept of feasibility or ΔG value to determine that the reaction is in a equilibrium or not $\Delta G = \Delta H - T\,\Delta S$

1. Calculate ΔG for the Reaction:

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$$

The standard free energy of glucose, CO_2 and H_2O are –910.5, – 394.4 , –237.2 respectively, show that it is feasible or not.

$$\Delta G = \Delta G_{product} - \Delta G_{reactant}$$

$$\text{Glucose} = -910.5$$
$$CO_2 = 6 \times -394.4$$
$$H_2O = 6 \times -237.2$$

$$\Delta G = [6 \times -394.4] + [6 \times -237.2] - 910.5 = -2879.1 \text{ kJ}$$

Therefore, reaction is feasible

$$\Delta H = \Delta H_{product} - \Delta H_{reactant}$$

$$\Delta S = \Delta S_{product} - \Delta S_{reactant}$$

Standard form of $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightarrow NH_3(g)$

$$\Delta H_f = -46.19 \text{ J/Mol}$$

The standard entropy

For, $N_2 = 191, H_2 = 130, NH_3 = 192$

$$\Delta S = \Delta S_{product} - \Delta S_{reactant} = 192 - \left[\frac{1}{2}\times 191 + \frac{3}{2}\times 130\right] = 192 - [95.5 + 195] = -98.5 \text{ J/K-mole}$$

$$T\Delta S = 298 \times (-98.5) = -29353 \text{ J/mole}$$

$$\Delta G = \Delta H_f - T\Delta S = -46.19 + (-29353) = -46.19 + 29353$$

$$= 29306.81 \text{ J/mol} = 29.306 \text{ kJ mol}^{-1}$$

Chemical Equilibrium:

The rate at which a substance reacts is proportional to its active mass and the rate of chemical reaction is directly proportional to product of active mass of reacting substance.

$$aA + bB \rightleftharpoons mM + nN$$

$$r_f \propto [A]^a [B]^b \text{ and } r_b \propto [M]^m [N]^n$$

$$r_f = k_f [A]^a [B]^b \text{ and } r_b = k_b [M]^m [N]^n$$

At equilibrium,

$$r_f = r_b$$

$$k_f [A]^a [B]^b = k_b [M]^m [N]^n$$

$$\frac{k_f}{k_b} = \frac{[M]^m [N]^n}{[A]^a [B]^b}$$

$$\Rightarrow \quad \frac{k_f}{k_b} = K_{eq}$$

$$\Rightarrow \quad K_{eq.} = \frac{k_f}{k_b} = \frac{[M]^m [N]^n}{[A]^a [B]^b}$$

The equilibrium candition can be written in terms of activity, partial pressure, molar concentration or mole fraction of the species involved in the reaction and K_{eq} will have different numerical value and different representation. The representation is K_a, K_p, K_c and K_x

Thermodynamic Treatment of Law of mass action

$$\Delta G = -RT \ln K_p$$

Consider the reaction, $aA + bB \rightleftharpoons mM + nN$

We know that chemical potential of a reaction consisting of 'a' mole of A and 'b' mole of B is given by

$$\frac{dG}{dn} = \mu_i$$

$$G_{reactant} = a \times \mu_A + b \times \mu_B$$

$$G_{product} = m \times \mu_M + n \times \mu_N$$

Change in Gibbs free energy

$$\Delta G = G_{product} - G_{reactant} = (m\,\mu_M + n\mu_N) - (a\,\mu_A + b\mu_B)$$

The chemical potential of i^{th} species

$$\mu_i = \mu_i^0 + RT \ln P_i \qquad \ldots (i)$$

Putting the value

$$\mu_M = \left[\mu_M^0 + RT \ln P_M\right], \mu_N = \left[\mu_N^0 + RT \ln P_N\right], \mu_A = \left[\mu_A^0 + RT \ln P_A\right]$$
$$\mu_B = \left[\mu_B^0 + RT \ln P_B\right]$$

$$\Delta G = m\left[\mu_M^0 + RT \ln P_M\right] + n\left[\mu_N^0 + RT \ln P_N\right] - a\left[\mu_A^0 + RT \ln P_A\right] - b\left[\mu_B^0 + RT \ln P_B\right]$$

At equilibrium, $\Delta G = 0$

$$0 = m\,\mu_M^0 + mRT \ln P_M + n\mu_N^0 + nRT \ln P_N - a\mu_A^0 - a\,RT \ln P_A - b\mu_B^0 - bRT \ln P_B$$

$$0 = m\,\mu_M^0 + RT \ln P_M^m + n\mu_N^0 + RT \ln P_N^n - a\mu_A^0 - RT \ln P_A^a - b\mu_B^0 - RT \ln P_B^b$$

$$-RT \ln P_M^m - RT \ln P_N^n + RT \ln P_A^a + RT \ln P_B^b = m\mu_M^0 + n\mu_N^0 - a\mu_A^0 - b\mu_B^0$$

$$-RT\left[\ln \frac{P_M^m\, P_N^n}{P_A^a\, P_B^b}\right] = \Delta G^0$$

$$\Rightarrow \quad \Delta G^0 = -RT\left[\ln \frac{P_M^m P_N^n}{P_A^a P_B^b}\right] \Rightarrow \frac{P_M^m P_N^n}{P_A^a P_B^b} = e^{-\Delta G^0/RT} \qquad \ldots (i)$$

$$\Rightarrow \quad \boxed{\Delta G = -RT \ln k_p} \qquad \ldots (ii)$$

where, $k_p = \dfrac{P_M^m\, P_N^n}{P_A^a\, P_B^b} = \text{constant}$

P_M, P_N, P_A and P_B be the partial pressure of component M, N, A and B.

The chemical potential in term of molar fraction (x_i)

$$\mu_i = \mu_i^0 + RT \ln x_i$$

From this the following expression analogous to equation (ii) is obtained.

$$k_x = \frac{x_M^m\, x_N^n}{x_A^a\, x_B^b}$$

and in term of molar concentrations (C_i)

$$\mu_i = \mu_i^0 + RT \ln C_i$$

From which we obtain that

$$K_C = \frac{[M]^m [N]^n}{[A]^a [B]^b}$$

If the reactants and the product are not ideal gases, then the equilibrium cosntants, K^{th},

$$K \equiv K^{th}\frac{\left(a_M^m a_N^n\right)}{\left(a_A^a\, a_B^b\right)}$$

where a_{is} are the activities. For non-ideal, i.e., real gases

$$K = K_f = \frac{\left(f_M^m\, f_N^n\right)}{\left(f_A^a\, f_B^b\right)}$$

where f_{is} are the fugacities. For a mixture of real gases,

$$r_i = \frac{f_i}{p_i} \text{ or } f_i = \gamma_i p_i, \text{ where } \gamma_{is} \text{ are the activity coefficients.}$$

Hence, $K_f = \frac{\gamma_M^m\, \gamma_N^n}{\gamma_A^a\, \gamma_B^b} \times \frac{P_M^m\, P_N^n}{P_A^a\, P_B^b}$

$$\boxed{K_f = K_\gamma\, K_p}$$

where, $K_\gamma = \frac{\gamma_M^m\, \gamma_N^n}{\gamma_A^a\, \gamma_B^b}$ and $K_p = \frac{P_M^m\, P_N^n}{P_A^a\, P_B^b}$

Van't Hoff reaction isotherm:

It readily follows

From equation (i) and (ii) that

$$K_p = e^{-\Delta G^0/RT} \quad or \quad \boxed{\Delta G = -RT \ln K_p}$$

Problem-3. Calculate K_p for the reaction, $CO_{(g)} + H_2O_{(s)} \rightarrow CO_2 + H_{2(g)}$

If ΔG for the reaction is 16.3 kJ/mol

Soln. $\Delta G = -RT \ln K_p \Rightarrow \log K_p = \frac{-16.3\times10^3}{8.314\times298\times2.303}$

$\log K_p = -28.5 \Rightarrow K_p = \text{anti}\log(-2.85)$;

$K_p = 1.41\times10^{-3}$

Relation between K_p, K_c and K_x:

$$aA + bB \rightleftharpoons mM + nN$$

$$K_p = \frac{p_M^m \times p_N^n}{p_A^a \times p_B^b} \qquad ...(1)$$

We know that, $P_M = x_M P$, $P_N = X_N P$

$P_A = x_A P$, $p_B = X_B P$

Putting value in equation (1)

$$K_p = \frac{(x_M P)^m (x_N P)^n}{(n_A P)^a (x_B P)^b} = \left[\frac{x_M^m\, x_N^n}{x_A^a\, x_B^b}\right] \times (P)^{(m+n)-(a+b)}$$

$\Rightarrow \quad \boxed{K_p = K_x P^{\Delta n}}$

$\Delta n = (m+n)-(a+b)$

At atmospheric pressure $\boxed{K_p = K_x}$

Relation between K_p and K_c :

$$PV = nRT \Rightarrow P = \frac{n}{V}RT \Rightarrow P = CRT \Rightarrow \boxed{p_i = C_iRT}$$

$$P_m = C_MRT;\ P_n = C_NRT;\ P_A = C_ART;\ P_B = C_BRT;$$

$$\therefore \quad K_p = \frac{(C_MRT)^m (C_NRT)^n}{(C_ART)^a (C_BRT)^b} = \left[\frac{C_M^m\, C_N^n}{C_A^a\, C_B^b}\right][RT]^{(m+n)-(a+b)}$$

$\Rightarrow \quad \boxed{K_p = K_c[RT]^{\Delta n}}$

Problem-4. Calculate K_c and K_x for the reaction, $N_2O_4 \rightleftharpoons 2NO_2(g)$ for which $K_p = 0.157$ atm.

Soln. $K_p = K_c[RT]^{\Delta n}$

$$\Rightarrow \quad K_c = \frac{K_p}{[RT]^{\Delta n}} = \frac{0.157}{0.0821 \times 300} = 6.37 \times 10^{-3}$$

Homogeneous Equilibria

There are two categories specified in the case of homogeneous equilibria.

(i) Number of mole of product are equal to the number of moles of reactant.

(ii) Number of product of mole doesn't equal to the number of reactant mole.

In Case-I:

$\Delta n_g = 0$; $K_p = K_c = K_x$

In this case the addition of inert gas to the reaction doesn't change the relative amount of the species.

	A	+	B	$\rightleftharpoons$	C	+	D
$t=0$	a		b		c		d
$t=t$	$a-x$		$b-x$		x		x

Total number of moles $= a+b$

$$\text{Partial pressure} = \frac{\text{number of mole}}{\text{total of moles}} \times P$$

$$\text{Partial pressure of A} = \left(\frac{a-x}{a+b}\right)P$$

$$\text{Partial pressure of B} = \left(\frac{b-x}{a+b}\right)P$$

Partial pressure of $C = \left(\frac{x}{a+b}\right)P$

Partial pressure of $D = \frac{x}{(a+b)}P$

$$K_p = \frac{\left(\frac{x}{a+b}\right)P \times \left(\frac{x}{a+b}\right)P}{\left(\frac{a-x}{a+b}\right)P\left(\frac{b-x}{a+b}\right)P} \Rightarrow \boxed{K_p = \frac{x^2}{(a-x)(b-x)}}$$

In Case-II :

Consider a case in which Δn is postive if $\Delta n_g \neq 0$

$$K_p \neq K_c \neq K_x$$

	A	$\rightleftharpoons$	B + C
t = 0	a		0 0
t = t	(a – x)		x x

Total number of moles = a + x

Partial pressure of A, $P_A = \left(\frac{a-x}{a+x}\right)P$

Partial pressure of B, $P_B = \left(\frac{x}{a+x}\right)P$

Partial pressure of C, $P_C = \left(\frac{x}{a+x}\right)P$

$$K_p = \frac{\left(\frac{x}{a+x}\right)P\left(\frac{x}{a+x}\right)P}{\left(\frac{a-x}{a+x}\right)P} \Rightarrow K_p = \frac{x^2}{\left(a^2-x^2\right)}P$$

In form of degree of dissociation:

If a = 1; $x = \alpha$

$$\boxed{K_p = \frac{\alpha^2}{\left(1-\alpha^2\right)}P}$$

Problem-5. $N_2O_4 \rightleftharpoons 2NO_2$. Find out K_p

Soln.

	N_2O_4	$\rightleftharpoons$	$2NO_2$
t = 0	1		0
t = t	(1 – α)		2α

Total number of moles $= 1-\alpha + 2\alpha = 1+\alpha$

$$K_p = \frac{(2\alpha)^2}{(1-\alpha^2)}P \Rightarrow K_p = \left(\frac{4\alpha^2}{1-\alpha^2}\right) \times P$$

Problem-6. The dissociation of PCl_5 was studied at 29°C at total pressure of 1 atm. The value of K_p is found. 0.46 calculate the degree of dissociation of PCl_5. If keeping the temperature constant the pressure of system is raised to 10 atm. what will be the degree of dissociation.

Soln.

	PCl_5	$\rightleftharpoons$	$PCl_3 + Cl_2$
$t=0$	1		0 0
$t=t$	$(1-\alpha)$		α α

Total number of moles $= 1-\alpha + 2\alpha = 1+\alpha$

Partial pressure of $PCl_5 = \left(\frac{1-\alpha}{1+\alpha}\right)P$

Partial pressure of $PCl_3 = \left(\frac{\alpha}{1+\alpha}\right)P$

Partial pressure of $Cl_2 = \left(\frac{\alpha}{1+\alpha}\right)P$

$$K_p = \frac{\left(\frac{\alpha}{1+\alpha}\right)P\left(\frac{\alpha}{1+\alpha}\right)P}{\left(\frac{1-\alpha}{1+\alpha}\right)P} \Rightarrow \boxed{K_p = \frac{\alpha^2 P}{(1-\alpha^2)}}$$

Given that, $K_p = 0.46$, $P = 1$, $\alpha = ?$

$$K_p = \frac{\alpha^2 \times 1}{(1-\alpha^2)} \Rightarrow (1-\alpha)^2 = \frac{\alpha^2}{0.46} \Rightarrow \alpha^2 = 0.46\,(1-\alpha^2)$$

$$\Rightarrow \quad \alpha^2 = 0.46 - 0.46\alpha^2 \Rightarrow \alpha^2\,[1+0.46] = 0.46$$

$$\alpha^2 = \frac{0.46}{1.46} \Rightarrow \alpha = \sqrt{\frac{0.46}{1.46}} \Rightarrow \alpha = 0.56$$

$K_p = 0.46$, $P = 10$, $\alpha = ?$

$$P \times \alpha^2 = 0.46(1-\alpha^2) \Rightarrow \alpha^2 = \frac{0.46 - 0.46\alpha^2}{10} \Rightarrow 0.46 - 0.46\,\alpha^2 = 10\alpha^2$$

$$\alpha^2 = 0.043 \Rightarrow \alpha = 0.02$$

We see that if we raise the pressure of the system lower the extent of dissociation.

Problem-7. The extent of dissociation of PCl_5 at a certain temp is 20% at 1 atm pressure calculate the pressure at which the substance is half dissociated at the same temperature.

Soln. $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

$$K_p = \frac{\alpha^2 P}{(1-\alpha^2)} = \frac{(0.2)^2 \times 1}{(1-(0.2)^2)}$$

$$K_p = \frac{0.04}{0.96} = \frac{1}{24} \simeq 0.04 \quad \text{... (i)}$$

$$K_p = \frac{\alpha^2 P}{(1-\alpha^2)} = \frac{(0.5)^2}{1-(0.5)^2} P_2$$

$$K_p = \left(\frac{0.025}{1\text{-}0.25}\right) P_2$$

$$K_p = \left(\frac{0.5}{0.75}\right) P_2 = 0.33 P_2 \quad \text{... (ii)}$$

Comparing equations (i) and (ii) we get

$$0.04 = 0.33\ P_2$$

$$P_2 = \frac{0.04}{0.33} = 0.12 \text{ atm}$$

Temperature Dependence of Equilibrium constant (Van't Hoff equation)

$$\Delta G = -RT \ln K_p$$

$$\ln K_p = -\frac{\Delta G^0}{RT}$$

$$\frac{d}{dT} \ln K_p = -\frac{1}{R}\left[\frac{d}{dT}\frac{\Delta G^0}{T}\right]$$

$$-R\left[\frac{d \ln K_p}{dT}\right] = \left[\frac{d}{dT}\left(\frac{\Delta G}{T}\right)\right] \quad \text{... (i)}$$

From Gibb's Helmholtz equation,

$$\left[\frac{d}{dT}\left(\frac{\Delta G}{T}\right)\right] = -\frac{\Delta H^0}{T^2} \quad \text{... (ii)}$$

From equation (i) and (ii), we get

$$\boxed{\left[\frac{d \ln K_p}{dT}\right] = \frac{\Delta H^0}{RT^2}}$$ Proved.

Where, ΔH^0 is the standard enthalpy of the reaction.

Integrated form of this equation:

$$\int \frac{d \ln K_p}{dT} = \int \frac{\Delta H^0}{RT^2} \quad \text{... (i)}$$

Integrate the Van't Hoff equation and determine the constant of integration

$$\int d \ln K_p = \int \frac{\Delta H^0}{RT^2} dT$$

$$\ln K_p = \frac{\Delta H}{R}\int \frac{1}{T^2}\,dT \qquad \left[\int \frac{1}{T^2} = dT \Rightarrow \int T^{-2}\,dT = \frac{T^{-2+1}}{-2+1} = -\frac{1}{T}\right]$$

$$\boxed{\ln K_p = \frac{-\Delta H^0}{RT} + I}$$

where, I is the constant of integration.

In standard condition it is consider that enthalpy doesn't depend on the temperature

$$\ln K_p = \frac{-\Delta H^0}{RT} + I \qquad \text{... (ii)}$$

$$\because \ln K_p = -\frac{\Delta G^0}{RT} \qquad \text{... (iii)}$$

From equation (ii) and (iii)

$$\frac{\Delta G^0}{RT} = \frac{\Delta H^0}{RT} - I \qquad \text{... (iv)}$$

$$\Rightarrow \quad \Delta G^0 = \frac{\Delta H^0}{RT} \times RT - I \times RT = \Delta H^0 - I \times RT$$

$$\Rightarrow IRT = T\Delta S \quad \Rightarrow I = \frac{\Delta S}{R} \qquad \text{... (v)}$$

From equation (iv) and (v), we obtain that,

$$\boxed{\Delta G^0 = \Delta H^0 - T\Delta S^0}$$

Integrated within limit:

If we integrate the equation (1) between two temperature T_1 and T_2, when the equilibrium constants are K_{p_1} and K_{p_2} respectively.

$$\int_{K_{p_1}}^{K_{p_2}} \frac{d\ln K_p}{dT} = \int_{T_1}^{T_2} \frac{\Delta H^0}{RT^2} \Rightarrow \ln \frac{K_{p_2}}{K_{p_1}} = \left[\frac{-\Delta H^0}{RT}\right]_{T_1}^{T_2} = \frac{-\Delta H^0}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] = \frac{\Delta H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\boxed{\ln \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H^0}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]}$$

Problem-8. The equilibrium constant of a reaction double on rising the temperature 25 to 35 calculate $\Delta H = ?$

Soln. Given that,

$$K_{p_1} = K, \; K_{p_2} = 2K, \; T_1 = 25^\circ C, \; T_2 = 35^\circ C$$

$$\ln \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H^0}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\ln\frac{2K}{K}=\frac{\Delta H^0}{8.314}\left[\frac{35-25}{35\times25}\right]\Rightarrow \ln 2=\frac{\Delta H^0}{8.314}\left[\frac{35-25}{35\times25}\right]$$

$$\log 2=\frac{\Delta H^0}{8.314}\left[\frac{308-298}{308\times298}\right]\Rightarrow \log 2=\frac{\Delta H^0}{2.303\times8.314}\left[\frac{10}{91784}\right]$$

$$\Delta H=\frac{.3010\times2.303\times8.314\times91784}{10}=52897.7\ J=52.89\ kJ$$

Problem-9. For the reaction:

$$CO+SO_3 \rightleftharpoons CO_2+SO_2$$

$$\Delta G = 187\ kJ/mole$$

$$\Delta H = 184\ kJ/mole \text{ at } 25^\circ$$

Calculate ΔG at 398 K and K_p at 398 K assuming that ΔH remains constant over the temperature interval.

Soln. $\frac{\partial(\Delta G/T)}{\partial T}=\frac{\partial H}{T^2}$ at 25°

$$d\left[\frac{\Delta G}{T}\right]=\left[\frac{\Delta H}{T^2}dT\right]\Rightarrow\left[\frac{\Delta G}{T}\right]_{\frac{\Delta G_1}{T_1}}^{\frac{\Delta G_2}{T_2}}=\left[\frac{-\Delta H}{T}\right]_{T_1}^{T_2}$$

Enthalpy and entropy is independent of temperature but ΔG dependent on temperature

$$\frac{\Delta G_{T_2}}{T_2}-\frac{\Delta G_{T_1}}{T_1}=-\left[\frac{\Delta H}{T_2}-\frac{\Delta H}{T_1}\right]=\frac{\Delta G_{398}}{398}-\frac{\Delta G_{298}}{298}=\Delta H\left[\frac{398-298}{398\times298}\right]$$

$$=\frac{\Delta G_{398}}{398}-\frac{187}{298}=+184\left[\frac{100}{398\times298}\right]$$

$$=298\times\Delta G_{398}-187\times398=184\times100$$

$$=298\times\Delta G_{398}=184\times100+187\times398$$

$$=18400+74426=298\times\Delta G_{391}=92826=56026$$

$$\Delta G_{398}=\frac{92826}{298}=311.5$$

$$\ln K_p=-\frac{\Delta G}{RT}\Rightarrow \log K_p=\frac{-311.5}{8.314\times2.303\times398}$$

then, $K_p=0.91$

Dependence of Equilibrium Constant

1. Dependence of K_P on the pressure :

Since ΔG depends upon the temperature alone. K_p also depends on the temperature alone and is independent of pressure.

Hence, $\frac{\partial \ln K_p}{\partial P}=0\Rightarrow\frac{-\partial}{\partial P}\left[\frac{-\Delta G}{RT}\right]=0$

2. Pressure dependence of K_C :

$$K_p = K_c[RT]^{\Delta n} \Rightarrow K_c = \frac{K_p}{[RT]^{\Delta n}} \Rightarrow K_c = K_p[RT]^{-\Delta n}$$

$$\ln K_c = \ln K_p - \Delta n \ln RT$$

$$\Rightarrow \frac{d}{dP}\ln K_c = \frac{d}{dP}\ln K_p - \frac{d}{dP}\Delta n \ln RT \Rightarrow \frac{d}{dP}\ln K_c = 0$$

i.e. K_c is also independent of pressure.

3. Pressure dependence of K_x :

$$K_p = K_x[P]^{\Delta n} \Rightarrow K_x = \frac{K_p}{(P)^{\Delta n}};\ K_x = K_p(P)^{-\Delta n} \Rightarrow \ln K_x = \ln K_p - \Delta n \ln P$$

differentiating both side above the equation,

$$\frac{d}{dP}\ln K_x = \frac{d}{dP}\ln K_p - \frac{d}{dP}\Delta n \ln P$$

$$\frac{d}{dP}\ln K_x = 0 - \frac{d}{dP}\Delta n \ln P \Rightarrow \frac{d}{dP}\ln K_x = -\Delta n\frac{1}{P}$$

$$\frac{d}{dP}\ln K_x = \frac{-\Delta n}{P} \qquad \ldots (1)$$

For ideal gas:

$$P\Delta V = \Delta nRT \Rightarrow \frac{\Delta n}{P} = \frac{\Delta V}{RT}$$

Put value in equation (1)

$$\boxed{\frac{d}{dP}\ln K_x = \frac{-\Delta V}{RT}}$$

where, $\Delta V = V_{product} - V_{reactant}$

when $\Delta n = 0$, K_x is pressure independent. when $\Delta n \neq 0$, then two case arises.

1. Case-I: $\Delta n > 0$

There is increase in the number of moles means $\Delta V > 0$

i.e. $\frac{d\ln K_x}{dP} = -\frac{\Delta V}{RT}$

K_x decrease with increase in pressure.

2. Case-II: $\Delta n < 0$

i.e. $\Delta V < 0$

K_x increases with increase in pressure.

Problem-1. 1 mole of PCl_5 is dissociated at pressure P and temperature T as follows:

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$ **[GATE]**

if degree of dissociation is 50% then,

(a) $P = 3K_p$ (b) $K_p = 3P$ (c) $P = \frac{3}{2}K_p$ (d) $K_p = \frac{3}{2}P$

Soln.

	$PCl_5 \rightleftharpoons$	PCl_3 +	Cl_2
Initially	1 mole	0	0
at equilibrium	$1-0.5$	0.5	0.5
	$=0.5$		

Total moles of equilibrium $= 0.5 + 0.5 + 0.5 = 1.5$

$$\therefore \quad P'_{PCl_5} = \frac{0.5}{1.5} \times P \quad \text{[if total pressure is P]}$$

$$P'_{PCl_3} = \frac{0.5}{1.5} \times P$$

$$P'_{PCl_2} = \frac{0.5}{1.5} \times P$$

Since, we know that,

$$K_p = \frac{P'_{PCl_3} \times P'_{Cl_2}}{P'_{PCl_5}} \Rightarrow K_p = \frac{\left(\frac{0.5}{1.5}\right)P \times \left(\frac{0.5}{1.5}\right)P}{\left(\frac{0.5}{1.5}\right)P}$$

$$\Rightarrow \quad K_p = \frac{0.5}{1.5}P = \frac{1}{3}P$$

Or, $\boxed{P = 3K_p}$

Correct answer is (a)

Problem-2. One mole of each of PCl_5, PCl_3 and Cl_2 are present at equilibrium in a vessel at 1 atm pressure, calculate K_p, given, $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ **[GATE]**

(a) $P = 3K_p$ (b) $P = 2K_p$ (c) $P = K_p$ (d) none of these

Soln.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

at equilbrium 1 1 1

Total moles $= 1 + 1 + 1 = 3$

Since, given, P = 1 atm

$$P'_{PCl_5} = \frac{1}{3}P \; ; \; P'_{PCl_3} = \frac{1}{3}P \; ; \; P'_{Cl_2} = \frac{1}{3}P$$

$$K_p = \frac{P'_{PCl_3} \times P'_{Cl_2}}{P'_{PCl_5}} \Rightarrow K_p = \frac{\frac{1}{3}P \times \frac{1}{3}P}{\frac{1}{3}P}$$

$K_p = \frac{1}{3}P$ or $\boxed{P = 3K_p}$

Correct answer is (a)

Problem-3. For the $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ at equilibrium. One mole of each present in a closed vessel of 1 litre volume.

It is found that equilibrium constant $\frac{1}{3}$. If concentration of each component is doubled, then equilibrium constant will be

(a) $\frac{1}{9}$ (b) $\frac{1}{6}$ (c) $\frac{1}{3}$ (d) 9

Soln. (c)

Because equilibrium constant does not depend upon concentration. So, the equilibrium constant is $\frac{1}{3}$ (which is given)

Problem-4. The equilibrium constant K_p for the reaction,

$H_2(g) + S(g) \rightleftharpoons H_2S(g)$ is 20.2 atm^{-1} at 945° and 9.1 atm^{-1} at 1065°C. Calculate ΔH^0.

Soln. According to the integrated van't hoff equation,

$$\ln\left(\frac{K_{p,2}}{K_{p,1}}\right) = \frac{\Delta H^0}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

Or, $$\Delta H^0 = R \ln\left(\frac{K_{p,2}}{K_{p,1}}\right)\left(\frac{T_1 T_2}{T_2 - T_1}\right)$$

$$\Rightarrow \quad \Delta H^0 = \left(8.314\ JK^{-1}mol^{-1}\right)\ln\left(\frac{9.21}{20.2}\right) \quad \left[\frac{(1218K)(1338K)}{1338K - 1218K}\right]$$

$$\Rightarrow \quad \Delta H^0 = -88126.3\ Jmol^{-1}$$

$$\Rightarrow \quad \Delta H^0 = -88.126\ kJ\ mol^{-1}$$

PRACTICE SET

1. An example of a reversible reaction is
(a) $Pb(NO_3)_2(aq) + 2NaI(aq) = PbI_2(s) + 2NaNO_3(aq)$
(b) $AgNO_3(aq) + HCl(aq) = AgCl(s) + HNO_3(aq)$
(c) $2Na(s) + 2H_2O(l) = 2NaOH(aq) + H_2(g)$
(d) $KNO_3(aq) + NaCl(aq) = KCl(aq) + NaNO_3(aq)$

2. For the reaction: $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$,
at a given temperature, the equilibrium amount of $CO_2(g)$ can be increased by
(a) adding a suitable catayst (b) adding a suitable catalyst
(b) decreasing the volume of the container (d) increasing the amount of CO(g)

3. At constant temperature, the equilibrium constant (K_p) for the decomposition reaction, $N_2O_4 \rightleftharpoons 2NO_2$, is expressed by $K_p = \frac{4x^2p}{(1-x^2)}$, where p = pressure, x = extent of decomposition. Which one of the following statements is true?
(a) K_p increases with increases of p (b) K_p increases with increases of x
(c) K_p increases with decreases of x (d) K_p remains constant with change n p and x

4. Consider the following equilibrium in a closed container $N_2O_4(g) \rightleftharpoons 2NO_2(g)$.
At a fixed temperature, the volume of the reaction container is halved. For this change, which of the following statements hold true regarding the equilibrium constant (K_p) and degree of dissociation (α)?
(a) Neither K_p nor α changes (b) Both K_p and α change
(c) K_p changes but α does not change (d) K_p does not change but α changes

5. $Ag^+ + NH_3 \rightleftharpoons [Ag(NH_3)]^+; k_1 = 3.5 \times 10^{-3}; [Ag(NH_3)]^+ + NH_3 \rightleftharpoons [Ag(NH_3)_2]^+; K_2 = 1.7 \times 10^{-3}$
then the formation constant of $[Ag(NH_3)_2]^+$ is
(a) 6.08×10^{-6} (b) 6.08×10^{6} (c) 6.08×10^{-9} (d) None of these

6. A mixture of 2 moles each of helium and an unknown gas (normal boiling point = 0°C) is kept in a 22.4 L flask. If the flask is cooled to 0.1 °C, the resultant pressure (in atm) inside the flask is
(a) 1.0 (b) 2.0 (c) 3.0 (d) 4.0

7. For the presumed equilibrium at 25°C, $A(g) + B(g) \rightleftharpoons C(g) + D(g)$ $\Delta H = -50$ kJ. The equilibrium constant of this process is:
(a) Shifted to the right by increasing the temperature.
(b) Shifted to the left by increasing pressure
(c) Unaffected by change in pressure
(d) Shifted to the right by increasing pressure

8. For the pair of reactions given below
(i) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ (ii) $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$
If at a particular temperature, K_{P1} and K_{P2} are the equilibrium constants for reactions (i) and (ii) respectively then,
(a) $K_{P_1} = 2K_{P_2}$ (b) $K_{P_1} = K^2_{P_2}$ (c) $2K_{P_1} = K_{P_2}$ (d) $K^2_{P_1} = K_{P_2}$

9. For the reaction: $Br_2(g)+BF_2(g)\longrightarrow 2BrF_3(g)$, the equilibrium constant at 2000 K and 1.0 bar is 5.25. When the pressure is increased by 8-fold, the equilibrium constant
(a) Increases by a factor of 1.86 (b) Decreases by a factor of 1.86
(c) Remains same (d) Increases by a factor of 8.

10. In a chemical reaction, $A(s)+B(g)\rightleftharpoons C(g)$
the total pressure at equilibrium is 6 atm. The value of equilibrium constant is:
(a) 1/2 (b) 9 (c) 1 (d) 36

11. Consider the reaction :
$A+B\rightleftharpoons C$
The unit of the thermodynamic equilibrium constant for the reaction is
(a) $mol\,L^{-1}$ (b) $L\,mol^{-1}$ (c) $mol^2\,L^{-2}$ (d) dimensionless

12. At a given temperature consider
$Fe_2O_3(s)+3CO(g)\rightleftharpoons 2Fe(s)+3CO_2(g);\ K_1=0.05$
$2CO_2(g)\rightleftharpoons 2CO(g)+O_2(g);\ K_2=2\times10^{-12}$
The equilibrium constant for the reaction
$2Fe_2O_3(s)\rightleftharpoons 4Fe(s)+3O_2$ is
(a) 1×10^{-13} (b) 2×10^{-38} (c) 4×10^{-15} (d) 2×10^{-24}

13. The relationship between the equilibrium constant K_1 for the reaction:
$$CO(g)+\frac{1}{2}O_2(g)\rightleftharpoons CO_2(g)$$
and the equilibrium constant K_2 for the reaction:
$$2CO(g)+O_2(g)\rightleftharpoons 2CO_2(g)$$ is:
(a) $2K_1=K_2$ (b) $K_1=K_2^2$ (c) $K_1=K_2$ (d) $K_1^2=K_2$

14. The hydrolysis constant (K_h) of NH_4Cl is 5.6×10^{-10}. The concentration of H_3O^+ in a 0.1 M solution of NH_4Cl at equilibrium is:
(a) $\sqrt{5.6\times10^{-11}}$ (b) $\sqrt{5.6\times10^{-10}}$ (c) 5.6×10^{-10} (d) 2.8×10^{-5}

15. The equilibrium constant Kc for the following reaction at 842°C is 7.90×10^{-3}. What is K_p at same temperature?
$$\frac{1}{2}F_2(g)\rightleftharpoons F(g)$$
(a) 8.64×10^{-5} (b) 8.26×10^{-4} (c) 7.90×10^{-2} (d) 7.56×10^{-2}

ANSWER KEY					
Questions	1	2	3	4	5
Option	(d)	(d)	(d)	(d)	(d)
Questions	6	7	8	9	10
Option	(d)	(c)	(b)	(c)	(c)
Questions	11	12	13	14	15
Option	(d)	(b)	(d)	(a)	(d)

Chapter 11

Phase Rule

Introduction

Phase is a homogenous, physically distinct and mechanically separable part of a system and is in dynamic equilibrium with the other parts (phases) through the transition of substances.

Explanation:

(1) Mixture of gases is always homogenous and constitute single phase i.e. P =1

$\underbrace{A_{(g)} + B_{(g)}}$ - P = 1

But if van der waal force of $A_{(g)} >> B_{(g)}$

liquify easily ↓ liquify hardly ↓

$\underbrace{\qquad\qquad}$ P = 2

(2) Colloidal solutions are heterogeneous
Therefore, P = number of solute + solvent

(3) True or aqueous solution is always homogenous, therefore, P = 1.

(4) Two polar solvents or non-polar solvent is always homogeneous, P = 1

$\underset{\text{Polar}}{H_2O_{(\ell)}} + \underset{\text{Polar}}{C_2H_5OH_{(\ell)}} \rightarrow$ Homogeneous

$\underset{\text{non-polar}}{CCl_{4(\ell)}} + \underset{\text{non-polar}}{C_2H_5 - O - C_2H_{5(\ell)}} \rightarrow$ Homogenous

But, $H_2O_{(\ell)} + CCl_{4(\ell)} \rightarrow$ not missible, P=2

polar non-polar (Heterogeneous)

(5) A gas in contact of a liquid generally constitute separate phase

$SO_{2(g)} + H_2O_{(\ell)} \rightarrow P = 2$

But as the dipole moment of gas increases solubility of gas in H_2O increases, P = 1

(i) $NH_{3(g)} + H_2O_{(\ell)} \rightarrow P = 1$

(ii) $HCl_{(g)} + H_2O_{(\ell)} \rightarrow P = 1$

(6) In saturated solution excess solid is in contact with aqueous solution , P = 2
e.g. Saturated solution of sugar.
Aqueous Sugar + Excess sugar → P = 2
(*l*) (*s*)

Below saturation only aqueous sugar P = 1

(7) In a mixture of solid ; P = number of solids.

e.g. $Fe_{(s)} + FeO_{(s)} + Fe_2O_{3(s)} \rightarrow P = 3$

(8) In an allotropic mixture

P = number of allotropes.

(9) An alloy is always homogeneous, P = 1

e.g. $\underbrace{Cu_{(s)} + Zn_{(s)}}_{\text{Brass (Homogenous)}} \longrightarrow P = 1$

(10) In a chemical reaction

P = different chemical substance

$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$ P = 3 (two solid + gas)

$NH_4Cl_{(s)} \rightleftharpoons \underbrace{NH_{3(g)} + HCl_{(g)}}_{\text{Homogenous(P=1)}}$ P = 2 (solid + gas)

e.g.

$\underbrace{H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}}_{\text{Homogenous}}$ P= 1

(11) Each hydrate in a solution constitute a phase.

e.g. $CuSO_4.5H_2O_{(s)} + CuSO_4.3H_2O_{(s)} + CuSO_4.H_2O_{(s)} + CuSO_{4(s)} + Ice_{(s)} + vapour_{(s)} \rightarrow P = 6$

Component (C):

The minimum number of constituents (i.e. molecular species) sufficient for determining the composition of all the phases of the system.

Every substance that can be separated from a system and exist outside of it, is called constituent

Number of component(c) = Constituent – equations relating them

(S) (R)

e.g. (i) $NH_4Cl_{(s)} \underset{R}{\rightleftharpoons} NH_{3(g)} + HCl_{(g)}$

Constitutent (s) = 3 (NH_4Cl, NH_3, HCl) & Equation (R) = 1

$\boxed{C = S - R}$

C = 3-1 = 2

(ii) In Ice $\underset{R}{\rightleftharpoons}$ water $\underset{R}{\rightleftharpoons}$ vapour

S = 3 and R = 2

Therefore, C = 3–2 = 1 i.e. one component.

(iii) $NH_4Cl_{(s)}$ is heated in a closed vessel.

$NH_4Cl_{(s)} \rightleftharpoons NH_{3(g)} + HCl_{(g)}$

S = 3

(a) NH_3 and HCl are present in equimolar ratio $[NH_3] = [HCl]$

R = 2 $\therefore$ C = 3–2 = 1

(b) If in the vessel NH_3 or HCl present

$[NH_3] \neq [HCl]$ $\therefore$ R = 1 $\Rightarrow$ C = 3-1 = 2

(iv) Mixture of gases which do not chemically combine (R = 0), component C = number of gases (Constituent) but Phase = 1

- Thus number of component is either equal to constituent (if $R = 0$) or less than it (If $R \neq 0$)
- If ions are also present, then in electroneutrality condition (positive ion = negative ion)

$$C = S - (R+1)$$

Degree of Freedom or variance (F) :

The minimum number of independent variables, such as temperature pressure and concentration which are utilised to characterize the system completely.

$$\boxed{F = C - P + 2}$$

$F = 0$ it is nonvariant or invariant

(e.g. **Triple point, Eutectic point and congruent point**)

$F = 1$, monovariant

$F = 2$ Bivariant etc.

$\Rightarrow$ P will be maximum when $F = 0$

$\therefore \quad 0 = C - P + 2 \Rightarrow \boxed{P_{max} = C + 2}$

(a) For one component system $C = 1$

$\therefore \quad P_{max} = 1 + 2 = 3$

(b) For two - component system $C = 2$

$$P_{max} = 2 + 2 = 4$$

$\Rightarrow$ F will be maximum when P = minimum (=1)

$\therefore \quad F_{max} = C - 1 + 2$ [P = 0 means system does not exist]

$$\boxed{F_{max} = C + 1}$$

Thus, C is increases F also increases

But P is increases then F also increases

$\Rightarrow$ If Equilibrium depends on electrical potential other than T and P.

$\boxed{F = C - P + 2 + \gamma}$ wher, γ = number of such variables

Problem-1. Calculate the number of phases, component and the number of degrees of freedom in following system.

(i) $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$, When $p_{NH_3} = p_{HCl}$

(ii) $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$, When $p_{NH_3} \neq p_{HCl}$

(iii) $I_2(s) \rightleftharpoons I_2(H_2O) + I_2(\text{Benzene})$

(iv) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

(v) Water at its freezing point.

(vi) water at its boiling point.

(vii) Aqueous solution of H_2SO_4.

(viii) Aqueous solution containing H_2SO_4 and acetic acid.

(ix) Aqueous solution of glucose.

(x) Sugar solution contained in an open beaker.

(xi) $Na_2SO_4.10H_2O \rightleftharpoons Na_2SO_4(s) + 10H_2O$

(xii) A beaker containing liquid water and sand.

(xiii) Liquid water and water vapour in equilibrium at 1 atm.

(xiv) $NH_4Cl(s) \rightleftharpoons NH_4Cl_{(vapour)} \rightleftharpoons NH_3(g) + HCl(g)$

(xv) $Sulphur_{(l)} \rightleftharpoons Sulphur_{(g)}$

(xvi) $Fe(s) + H_2O(g) \rightleftharpoons FeO(s) + H_2(s)$

(xvii) Solid camphor in equilibrium with its vapour

(xviii) Binary azeoptropic liquid mixture.

(xix) A subtance at critical point.

(xx) A substance above critical point.

Soln. (i) P = 2 (solid NH_4Cl + gas mixture of $(NH_3 + HCl)$

C = 3–2 = 1 $\therefore$ F = 1–2+2 = 1

(ii) P = 2, C = 3–1 = 2 $\therefore$ F = 2–2+2=2

(iii) P = 3 $(I_{2(s)} + H_2O_{(l)} + Benzene_{(l)})$

C = 3– 0 = 3 (Actually there is no equilibrium (R = 0) between $I_2(s)$, $I_{2\ (H2O)}$ and $I_{2\ (Benzene)}$

F = 3 – 3 + 2 =2

(iv) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

P = 3, C = 3 – 1 = 2

F = 2 – 3 +2 = 1

(v) At freezing point ice $\rightleftharpoons$ water $\rightleftharpoons$ vapour

P = 3, C = 3 – 2 =1

F = 1 - 3 + 2 = 0 (non variant)

(vi) At boiling point water $\rightleftharpoons$ vapour

P = 2, C = 2– 1 = 1 F = 1

(vii) P = 1 (Homogenous soln. of $H_2SO_4 + H_2O$)

C = 2, F = 3

(viii) Aqueous $H_2SO_4 + CH_3COOH$
(not miscible)

C = 3, P = 2, F = 3 .

(ix) P = 1, C = 2, F = 3

(x) Container does not constitute phase

P = 1, C = 2, F = 3

(xi) P = 3 $(Na_2SO_4.10H_2O(s), Na_2SO_4(s)$ and $H_2O(\ell))$

C = 3 – 1 = 2

F = 1

(xii) Sand does not constitute phase as there is no exchange of any chemical species between sand and other phase.

P = 2 (water and its vapour)

C = 1 $\therefore$ F = 1

(xiii) At constant 'P' reduced phase rule $F = C - P + 1$ used

$P = 2 \quad C = 1; \; F = 1 - 2 + 1 = 0$

(xiv) $P = 2$ (NH_4Cl solid and gaseous phase)

$C = 1$ (when $p_{NH_3} = p_{HCl}$) $\quad F = 1$

If $p_{NH_3} \neq p_{HCl}$

$C = 2, \quad F = 2$

(xv) $P = 2, \; C = 2 - 1 = 1 \qquad \therefore F = 1$

(xvi) $P = 3$ ($FeO_{(s)}$, $Fe_{(s)}$ and gas phase)

$C = 4 - 1 = 3 \quad \therefore \; F = 2$

(xvii) $P = 2, \quad C = 1 \qquad \therefore \; F = 1$

(xviii) In azeotropic mixture composition of liquid and vapour phase are same, thus composition remains constant and reduced phase rule is used.

$P = 2 \quad , \; C = 2$

$\therefore \qquad F = C - P + 1 = 2 - 2 + 1 = 1$

(xix) At critical point water $\rightleftharpoons$ liquid

or

(gas) (R=1)

$P = 2, \quad C = 2 - 1 = 1$

$F = C - P + 1$ [At critical point liquid and vapour phase are identical]

$F = 0$ (Invariant)

(xx) Above critical point only gas present and behaves ideally

$P = 1, \qquad C = 1 \qquad F = C - P + 2 = 2$

Problem-2. Determine number of component for following.

(i)- $NaCl_{(s)}, KCl_{(s)} \; Na^+_{(aq)} \; K^+_{(aq)} \; Cl^-_{(aq)}, H_2O_{(\ell)}, H_2O_{(g)}$

(ii) $CaCl_2.6H_2O_{(s)}, Ca^{++}_{(aq)}, Cl^-_{(aq)} \; H_2O_{(\ell)} \; H_2O_{(g)}$

Soln. (i) (a) In electroneutrality condition

$$NaCl_{(s)} + KCl_{(s)} + H_2O_{(\ell)} \rightarrow K^+_{(aq)} + Na^+_{(aq)} + 2Cl^+_{(aq)} + H_2O_{(g)}$$

(b) $NaCl \rightleftharpoons Na^+ + Cl^-$

(c) $KCl \rightleftharpoons K^+ + Cl^-$ $\qquad S = 7, \; R = 4$

(d) $H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$

Component (c) $= 7 - 4 = 3$

(ii) $CaCl_2.6H_2O_{(s)}, Ca^{++} + 2Cl^-, \; H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$

$S = 5$ and $R = 1$

$C = 5 - 1 = 4$

Phase Transition:

In a system of various phases, at equilibrium transition of substance between various phases takes place and Clapeyron equation is applicable.

$$\frac{dP}{dT} = \frac{\Delta H}{T(V_2 - V_1)}$$

ΔH = Heat of phase transformation.
v_1 = molar volume of pure substance in phase 1
v_2 = molar volume of pure substance in phase 2

First order Phase transition :

Clayperon equation is applicable and only one variable temperature or pressure or concentration is used to define a system.
Melting, vaporisation, sublimation etc.

Melting: ΔH_f = +ve (Heat absorbed for melting)

$$\text{Solid} \rightleftharpoons \text{liquid}$$
$$(V_s) \qquad (V_l)$$

(a) If $V_s > V_\ell$ $\qquad V_\ell - V_s = -ve$

$$\therefore \quad \frac{dP}{dT} = \frac{\Delta H}{T_f\left(V_\ell - V_s\right)}$$

Thus RHS = negative

$$\frac{dP}{dT} = -ve.$$

Thus on increases pressure m.p. of decreases ice. e.g. ice, Bismuth, Gallium

(b) If $V_l > V_s$, $V_l - V_s = +ve$

$$\frac{dP}{dT} = +ve.$$

Thus on increases pressure m.p. increases etc. e.g. CO_2 and majority of substance.

Vaporisation:

$$\text{Liquid} \rightleftharpoons \text{vapour}$$
$$(V_l) \qquad (V_g)$$

ΔH_v = +ve (Enthalpy of vaporisation)

Since $V_g >> V_l$

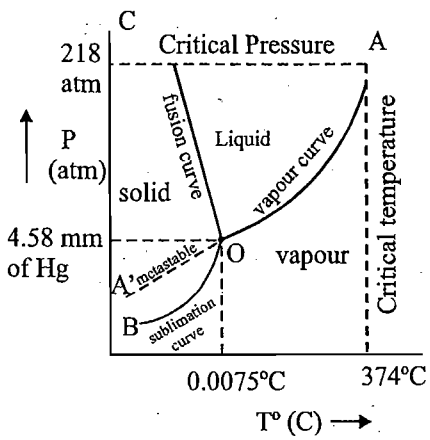
$$\therefore \quad \frac{dP}{dT} = +ve.$$

Thus, on increasing pressure boiling point increases

Phase Diagram:

[A] One component system:

Phase diagram of H_2O:



It consist of three parts.
(1) Areas
(2) Curves
(3) Points

Areas :

AOB, AOC and BOC only gas, liquid and solid exists respectively.

$\therefore \quad P = 1, \quad C = 1$

$F = C - P + 2 = 1 - 1 + 2 = 2$ (Bivariant)

Thus two variable are needed to define a point in these areas.

Curves:

(i) $OC = \underset{(ice)}{solid} \overset{fusion}{\rightleftharpoons} \underset{(water)}{liquid}$

(ii) $OA = \underset{(water)}{liquid} \overset{vaporization}{\rightleftharpoons} \underset{(gas)}{vapour}$

(iii) $OB = \underset{(ice)}{solid} \overset{sublimation}{\rightleftharpoons} \underset{(gas)}{vapour}$

Along these curves $P = 2,\ C = 2-1 = 1$

$\therefore \quad F = 1-2+2 = 1, (\text{Mono variant})$

Thus either temperature or pressure needed to locate the point in these curves.

Point:

At point 'O' three phases co-exist in equilibrium.

$$ice \rightleftharpoons water \rightleftharpoons vapour$$

$P = 3,\ C = 3-2 = 1,\ \therefore F = 1-3+2 = 0$ (non variant)

The point 'O' is called 'triple point' and is non variant.

At triple point $P = 4.58$ mm of Hg.

$T = .0075°C$

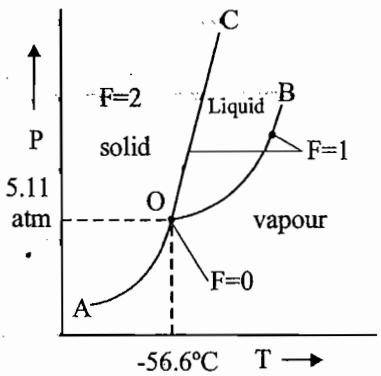
Along OA' super cooled liquid will exist in equilibrium with its vapour. [A liquid below its freezing point in liquid from called super cooled liquid]

In presence of ice or other impurity supercooled liquid changes into solid ice and curve OA' merges into OB.

Along metastable curve $F = 1$ (univariant)

Phase diagram of CO_2:

The phase diagram of CO_2 is similar to that of H_2O except towards the behaviour of fusion curve.



In CO_2 $V_s < V_\ell$

$$\therefore \quad \frac{dP}{dT} = \frac{\Delta H}{T_f (V_\ell - V_s)} \qquad (\Delta H = +ve)$$

$\frac{dP}{dT} = +ve$ Thus on increasing pressure boiling point increases

But in H_2O $V_s > V_\ell$

$$\therefore \quad \frac{dP}{dT} = -ve$$ if P increases boiling point decreases

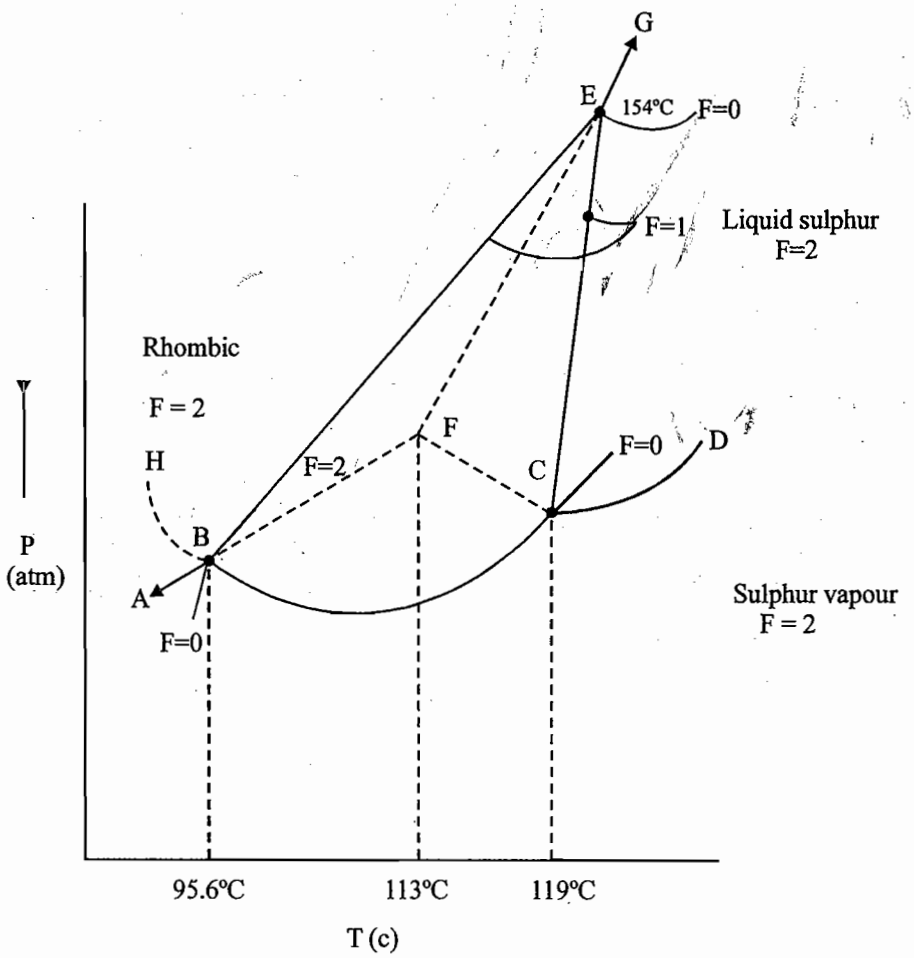
Phase diagram of sulphur:

Sulphur exists in four phases:

(i) Rhombic (S_R) (ii) Monoclinic (S_M)

(iii) Liquid sulphur(S_L) (iv) Sulphur vapour (S_V)

But all the phases does not exist in equilibrium. P = 4, C = 1 then F = –1 (meaningless)
Thus only three phases exist in equilibrium.



The diagram consists of

(i) **Curves:** Six stable curves AB, BC, CD, CE, EG and BE. Four metastable curves, BH, BF, CF and EF.

(ii) **Points:** B, C, E and F

(iii) **Areas:** Four Areas, namely ABEG, ABCD, GECD and BCE.

Description:

(i) (a) Stable curves.

AB, $S_R \rightleftharpoons S_V$	Sublimation curve of S_R.
BC, $S_M \rightleftharpoons S_V$	Sublimation curve of S_M.
CD, $S_L \rightleftharpoons S_V$	Vaporisation curve of S_L.
CE, $S_M \rightleftharpoons S_L$	Fusion curve of S_M.
EG, $S_R \rightleftharpoons S_L$	Fusion curve of S_R.
BE, $S_R \rightleftharpoons S_M$	Transition curve of S_R.

(b) Metastable Curve:

BH = metastable sublimation curve of S_M.($S_M \rightleftharpoons S_V$)

BC = metastable sublimation curve of S_R. ($S_R \rightleftharpoons S_V$)

CF = metastable curve of supercooled S_L. ($S_L \rightleftharpoons S_v$)

EF = metastable fusion curve of S_R. ($S_R \rightleftharpoons S_L$)

Along all these curves $P = 2, C = 1$

Therefore, $F = C - P + 2 = 1 - 2 + 2 = 1$ (Monovariant)

(ii) **Points:**

Point B, C and E are 3 triple point and F is metastable triple point.

At point B, $S_R \rightleftharpoons S_M \rightleftharpoons S_V$

At point C, $S_M \rightleftharpoons S_L \rightleftharpoons S_V$

At point E, $S_R \rightleftharpoons S_M \rightleftharpoons S_L$

At metastable point, $S_R \rightleftharpoons S_L \rightleftharpoons S_V$

Thus along triple point $P = 3, \quad C = 1$

$F = 0$, (Triple points are invariant)

(iii) Along areas only S_R, S_M, S_V and S_L present.

$\therefore \quad P = 1, \quad C = 1, \quad F = 2$ (Bivariant)

Note: $S_R \underset{}{\overset{95.6°C}{\rightleftharpoons}} S_M$

Thus 95.6°C is transition temp. of S_R.

(i) At room temp. (25°C) below 95.6°C S_R will exist. [$P = 1, C = 1, F = 2$]

(ii) Above 95.6°C S_M will exist. [$P = 1, C = 1, F = 2$]

At 95.6°C $P = 2, C = 1, \therefore F = 1$

Two Component system:

For two component system the phase rule becomes, $F = C - P + 2 \Rightarrow F = 4 - P$

The minimum number of the phases, P in the system is 1.

If $P = 1$, then F will be maximum

Therefore, for two component system.

$$F_{max} = 2 - 1 + 2 = 3$$

The maximum number of the degree of freedom, F is 3.

Thus 3 variables temperature, pressure and compositions are used to locate a point.

Thus phase diagram would be 3D or space model. This can't be represented on paper. Thus one variable is kept constant.

Generally P = constant and phase diagram is 2D temperature - concentration diagram.

Reduced phase Rule:

Since, P = constant.

$F = [C - P + 2] - 1$ (Removing one variable)

$$\boxed{F = C - P + 1}$$

There are 2 cases for 2-component system.

(i) Two components are completely miscible.

(ii) Two components are completely immiscible.

Two component completely miscible

3 types

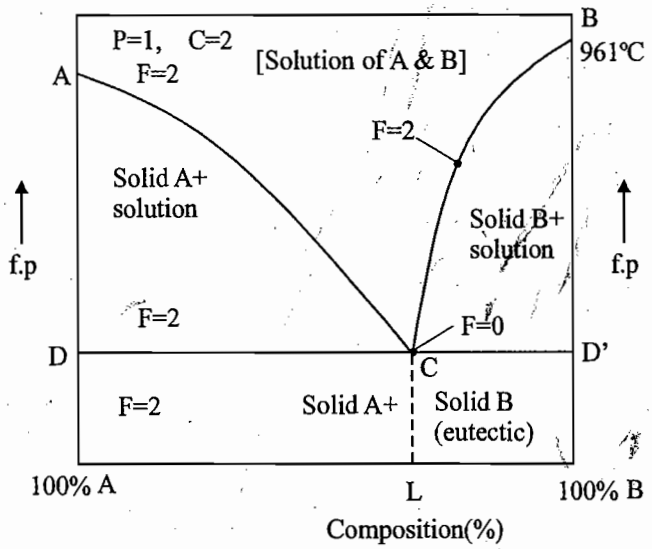
Eutectic formation	Congruent m.p.	Incongruent m.p.

Eutectic Systems (Eutectic = Easy melting):

A liquid mixture of two components, which has lowest freezing point (thus easily melt) compared to all other liquid mixtures and on cooling such a mixture, both the components separate out as solid phases.

The temperature at eutectic point is called eutectic temperature (T_E).

General Phase Diagram of Eutectic system



A = freezing point of pure A

B = freezing point of pure B

C = Eutectic point

L = Eutectic composition.

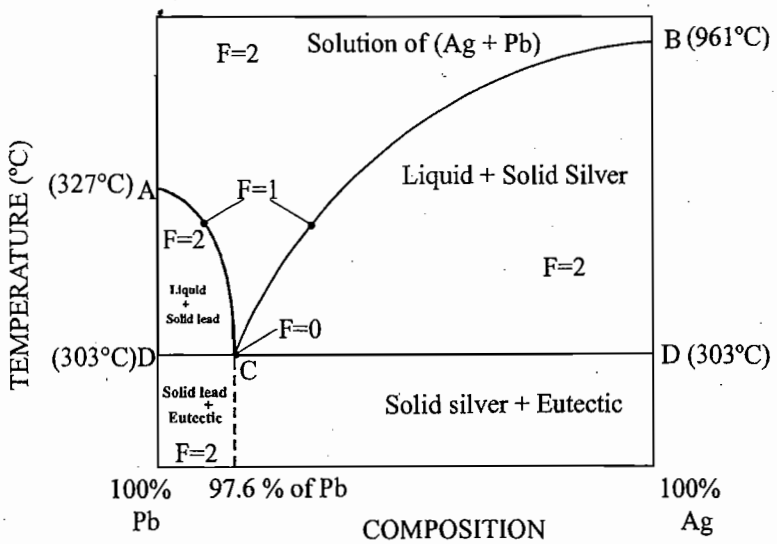
In Eutectic mixture component do not enter into chemical combination and separate crystals can be seen under microscope.

Silver - Lead System:

AC = freezing point curve of Pb. Addition of solution along AC lowers the freezing point of Pb.

BC = freezing point curve of Ag

C = Eutectic point



Areas:

(i) The region above ACB contains miscible solution.

$P = 1, \quad C = 2$

$F = C - P + 1 = 2 - 1 + 1 = 2$ (Bivariant)

(ii) Region ADC and BD'C contain pure Pb and Ag in equilibrium with solution

$\therefore \quad P = 1, C = 2, F = 2$ (Bivariant)

Curves:

AC, solid Pb $\rightleftharpoons$ solution

BC, solid Ag $\rightleftharpoons$ solution

$\therefore \quad P = 2, \quad C = 2, \quad \therefore F = C - P + 1$

$F = 2 - 2 + 1 = 1$ (univariant)

Eutectic Point (C):

Three phases coexist (solid Ag, solid Pb and solution)

$P = 3, \quad C = 2$

$\therefore \quad F = C - P + 1 = 2 - 3 + 1 = 0$ (nonvariant)

Thus eutectic point has fixed temperature and composition. Above eutectic (300°C) solution exist and below E_T pure solids along eutectics exist.

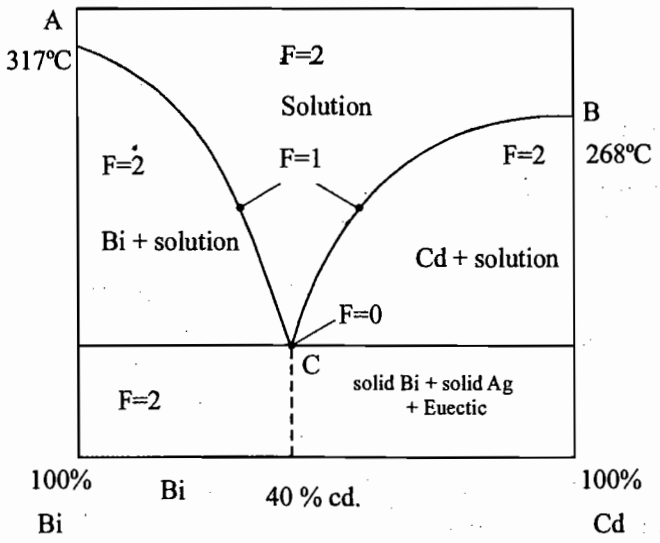
Along with DD'O'O pure substance exist. It is bivariant.

Importance of Pb - Ag system:

It forms the basis of pattinson's process for desilverisation of lead.

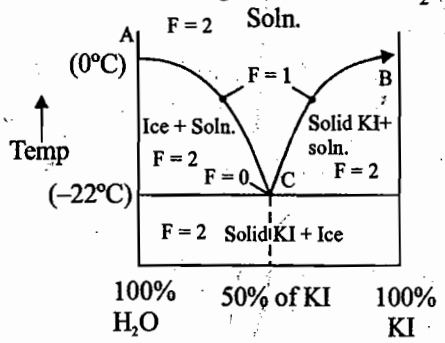
On cooling the mixture, Pb seperates out as pure solid due to low freezing point (327°C) thus remaining solution be richer in Ag. On further cooling upto eutectic temperature the solution becomes 2.4% of Ag.

Bismuth-cadmium system:



KI-H_2O System:

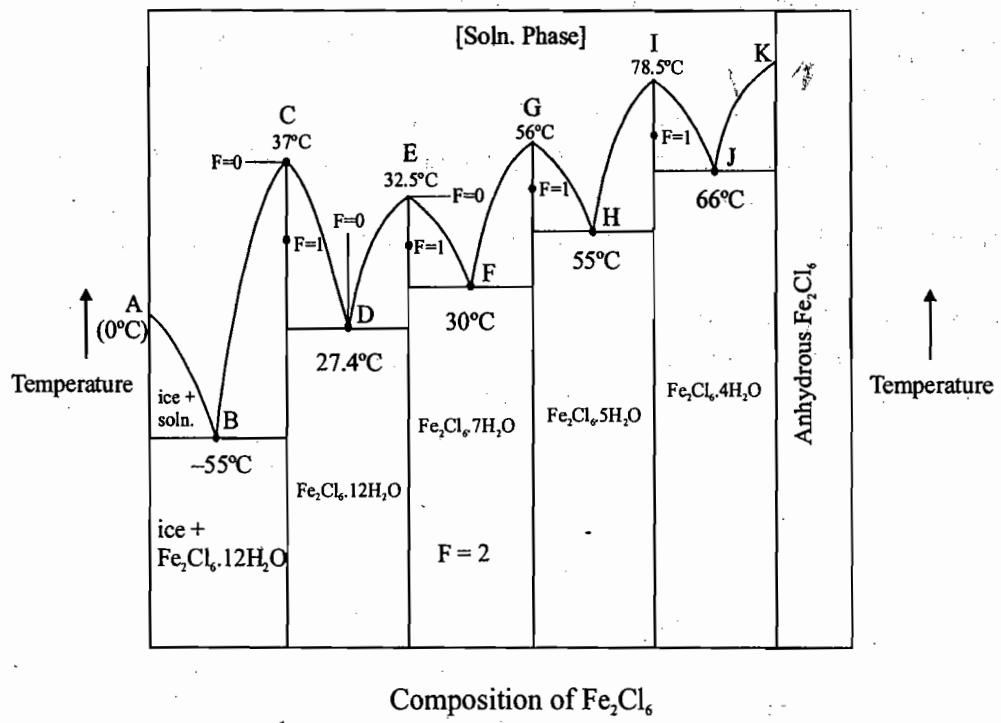
B do not reach on Y-coordinate because the two component KI and H_2O are not completely miscible.



System with congruent melting point:

The compound which completely melts at a constant temperature and the liquid state has same composition as that of the solid is called congruent melting compound. The temperature at this point is called congruent melting point or dystactic point.

$FeCl_3$-H_2O-System:



Composition of Fe_2Cl_6

(1) **Eutectic points:** B, D, F, H, J. (minima)

$P = 3, \quad C = 2, \quad F = C - P + 1$

$= 2 - 3 + 1 = 0$ (non variant)

(2) **Congruent melting point:** Maxima C, E, G and I

$P = 3, \quad C = 2 \quad \therefore \quad F = 0$ (non variant)

(3) **Curves:**

A is freezing point of water (0°C). Addition of Fe_2Cl_6 lower freezing point to –55°C.

BCD solubility curve of $Fe_2Cl_6.12H_2O$.

DEF solubility curve of $Fe_2Cl_6.7H_2O$

FGH solubiltiy curve of $Fe_2Cl_6.5H_2O$

HIJ solubility curve of $Fe_2Cl_6.4H_2O$.

Along curves $P = 2, \quad C = 2, F = 1$ (monovariant)

(4) **Areas:** Area above and below ABCDEFGHIJ

$P = 1, \quad C = 2 \quad F = 2(\text{bivariant})$

Vapour Pressure-Composition Diagram of a Binary Liquid Solution

Application of Phase rule:

(a) System consisting of only one phase

(b) System consisting of two phases: If the system has two phases in equilibrium, namely, liquid and vapour, then the variance of the system is two. This means that the values of only two variables will have to be stated in order to describe the system completely. Any two of the three variables, temperature, pressure and composition can be stated. The third one automatically will have a definite value.

The straight line of Figure-(1) and and the curved line of Figure- (2) represent the two phases, liquid and vapour, in equilibrium with each other.

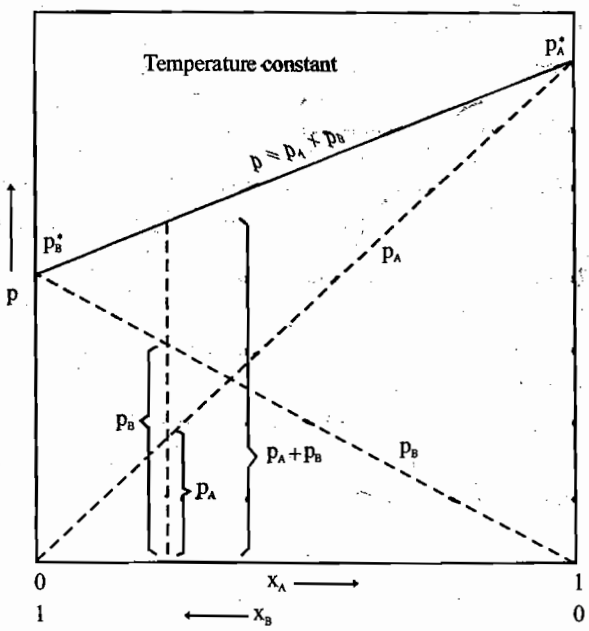


Figure - (1)

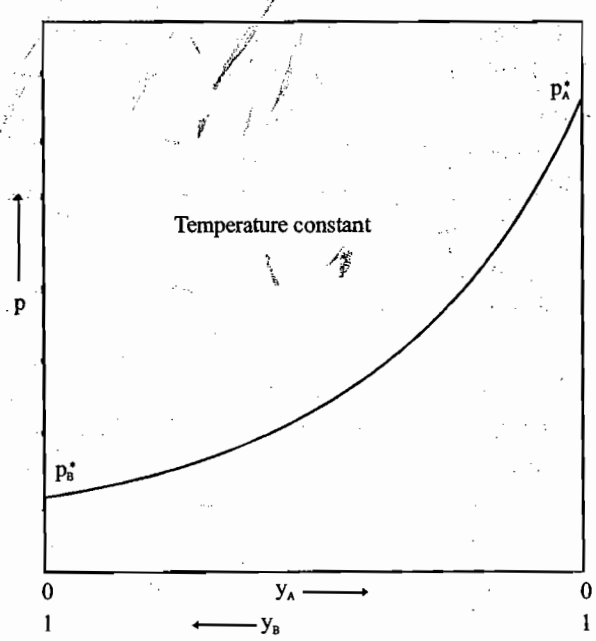


Figure - (2)

The two states, namely, liquid and vapour, can be shown in one diagram. This is shows in figure-(3)

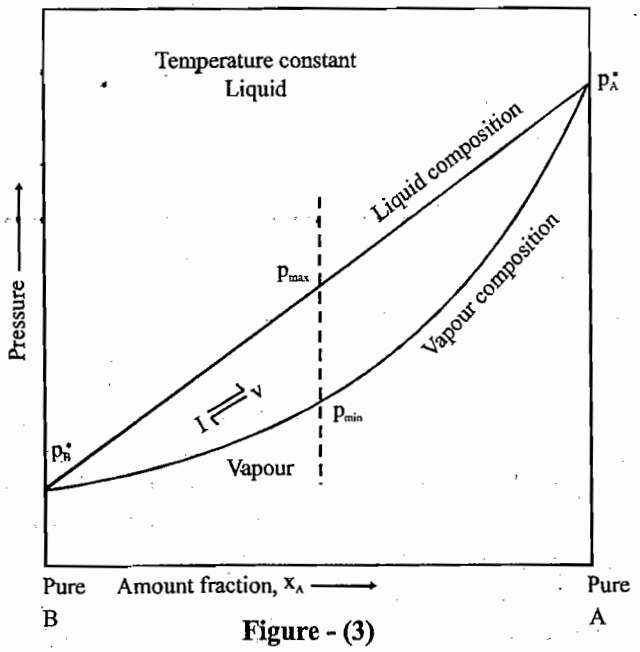


Figure - (3)

The upper curve is called the liquidus curve since this represents the line above which only liquid phase exists. A point anywhere on this line represents the two phases, liquid and vapour, in equilibrium with each other. Similarly, the lower curve is called the vaporous curve since it represents the curve below which only vapour exsits. Along this line, also the two phases liquid and vapour, are in equilibrium with each other.

A point anywhere in the region between the two curves represents the system in which both liquid and vapour coexist in equilibrium with each other. It is for this reason, this region is known as the liquid-vapour region. For a given composition, the points on the liquidus and vaporous curves represents, respectively, the maximum and the minimum pressures within which the two phases can exist in equilibrium with each other. The above facts can be summarized as follows.

(i) If $p_{system} > p_{max}$; only liquid phase exists.
(ii) If $p_{system} < p_{min}$; only vapour phase exists.
(iii) For $p_{max} > p_{system} > p_{min}$; the liquid and vapour phases are in equilibrium with each other

Tie Line: As indicated above, the region between the liquids and vaporous curves of Figure-(3) represents a region where both the phases exist in equilibrium with each other. For this region, P = 2 and thus F = 2. Since the temperature is fixed, one other variable (any one of p, x_A and y_A) is sufficient to describe the system completely. For instance, if p is chosen, then the amount fractions of the component A in the liquid and vapour phases are represented by the intersection points of a horizontal line, known as tie line, drawn from the given 'p' with those of liquidus and vaporous curves, respectively. If x_A is chosen as the describing variable, then the intersection of a vertical line from x_A with the liquidus curve yields the value of p and a horizontal line from p cutting the vaprous curve gives the vapour composition y_A.

The Lever Rule: A point within the liquid and vapour curves represents two phases, liquid and vapour, in equilibrium with each other. For the point a shown in Figure-(4). The amount fraction of the constituent A in the liquid phase is given by the point b (i.e. x_A) and the that in the vapour phase is given the point c (i.e. y_A)

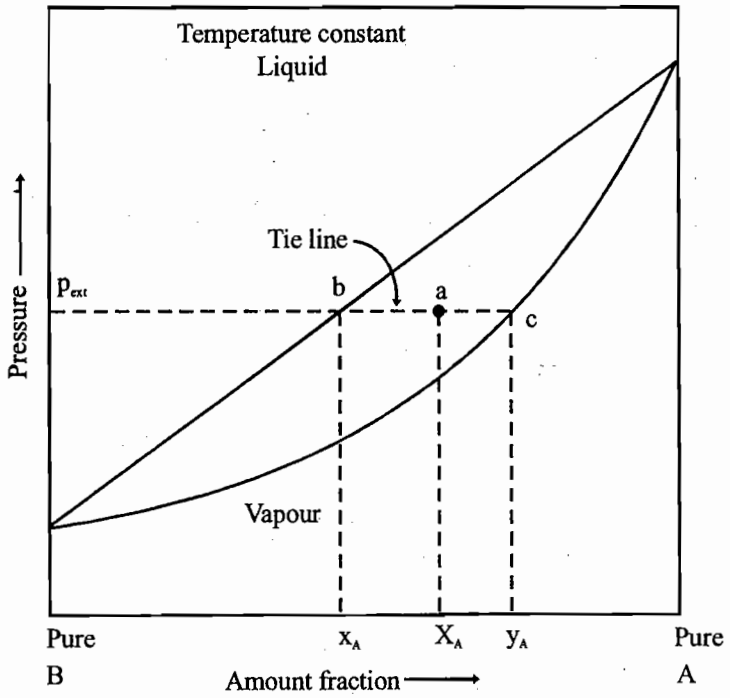


Figure - (4)

Thus, if the point 'a' is nearer to 'b', the system will consist of a larger amount of liquid and a relatively smaller amount of vapour, but if it is nearer to 'c', then the amount of liquid present is relatively small as compared with the amount of vapour present. As a moves from 'b' to 'c', more and more of the vapour is formed, thus the distance 'ab' represents the amount of vapour formed. Similarly, as a moves from 'c' to 'b', more and more of the liquid is formed and thus the distance 'ac' represents the amount of liquid formed. Taking these together, we have

distance ab $\propto$ amount of the vapour formed
distance ac $\propto$ amount of the liquid formed.

Taking the ratio, we have

$$\frac{ab}{ac} = \frac{\text{amount of the vapour formed}}{\text{amount of the liquid formed}} \quad \ldots (1)$$

Equation (i) is knows as the lever rule.

Quantitative derivation of the lever rule: The amount fraction X_A corresponding to the point a represents the amount fraction of the component A in the entire system consisting of liquid and vapour phases, i.e.

$$X_A = \frac{n_{A(l)} + n_{A(v)}}{n_{A(l)} + n_{A(v)} + n_{B(l)} + n_{B(v)}} \quad \ldots (2)$$

From Figure-(4), we have

$$(ab) = X_A - x_A = X_A - \frac{n_{A(l)}}{n_{A(l)} + n_{B(l)}} \quad \ldots (3)$$

$$(ac) = y_A - X_A = \frac{n_{A(v)}}{n_{A(v)} + n_{B(v)}} - X_A \quad \ldots (4)$$

Multiplying equation (3) by $n_{A(l)} + n_{B(l)}$ and equation (4) by $n_{A(v)} + n_{B(v)}$, we have

$$\left(n_{A(l)} + n_{B(l)}\right)(ab) = \left(n_{A(l)} + n_{B(l)}\right)X_A - n_{A(l)} \quad \ldots (5)$$

$$\left(n_{A(v)} + n_{B(v)}\right)(ac) = n_{A(v)} - \left(n_{A(v)} + n_{B(v)}\right)X_A \quad \ldots (6)$$

Subtracting equation (6) from equation (5) becomes

$$\left(n_{A(l)} + n_{B(l)}\right)(ab) - \left(n_{A(v)} + n_{B(v)}(ac)\right) = x_A\left(n_{A(l)} + n_{B(l)} + n_{A(v)} + n_{B(v)}\right) - \left(n_{A(l)} + n_{A(v)}\right)$$

Which on making use of equation (2) becomes,

$$\left(n_{A(l)} + n_{B(l)}\right)(ab) - \left(n_{A(v)} + n_{B(v)}(ac)\right) = 0$$

Or, $$\left(\frac{ab}{ac}\right) = \frac{n_{A(v)} + n_{B(v)}}{n_{A(l)} + n_{B(l)}}$$

i.e. $$\left(\frac{ab}{ac}\right) = \frac{\text{amount in the vapour phase}}{\text{amount in the liquid phase}}$$

Problem-1. At 353 K, the vapour pressures of pure ethylene bromide and propylene bromide are 22.93 and 16.93 kN m^{-2}, respectively, and these compounds form nearly ideal solution. 3 mol of ethylene bromide and 2 mol of propylene bromide are equilibrated at 353 K and a total pressure of 20.4 kN m^{-2}.

(a) What is the composition of the liquid phase?

(b) What amount of each compound is present in the vapour phase?

Soln. The given that

$$p_A^* = p^*_{\underset{\text{bromide}}{\text{ethylene}}} = 22.93 \text{ kN m}^{-2} \text{ and } p_B^* = p^*_{\underset{\text{bromide}}{\text{propylene}}} = 16.93 \text{ kN m}^{-2}$$

$$n_A = 3 \text{ mol}, \; n_B = 2 \text{ mol}, \; p = 20.4 \text{ kN m}^{-2}$$

(a) We have, $p = p_A + p_B = x_A p_A^* + x_B p_B^* = p_B^* + \left(p_A^* - p_B^*\right) x_A$

Therefore, $x_A = \dfrac{p - p_B^*}{p_A^* - p_B^*}$

Substituting the given data, we have

$$x_A = \frac{20.4\ \text{kN m}^{-2} - 16.93\ \text{kN m}^{-2}}{22.93\ \text{kN m}^{-2} - 16.93\ \text{kN m}^{-2}} = 0.578$$

$$x_B = 1 - 0.578 = 0.422$$

(b) Now, $y_A = \dfrac{p_A}{p} = \dfrac{x_A p_A^*}{p} = \dfrac{0.578 \times 22.93\ \text{kN m}^{-2}}{20.4\ \text{kN m}^{-2}} = 0.65$

Let n_A and n_B be the amounts of vaporized ethylene bromide and propylene bromide, respectively, when p = 20.4 kN m^{-2}. Hence, we have

$$y_A = \frac{n_A}{n_A + n_B} = 0.6497$$

$$x_A = \frac{3\ \text{mol} - n_A}{(3\ \text{mol} - n_A) + (2\ \text{mol} - n_B)} = \frac{3\text{mol} - n_A}{5\ \text{mol} - (n_A + n_B)} = \frac{3\ \text{mol} - n_A}{5\ \text{mol} - n_A/0.65} = 0.57$$

Or, $$(3\ \text{mol} - n_A) = 0.57\left(5\ \text{mol} - \frac{n_A}{0.65}\right)$$

Therefore, $$n_A = \frac{3\ \text{mol} - 0.58 \times 5\ \text{mol}}{1 - 0.58/0.65} = 0.99\ \text{mol}$$

Since, $\dfrac{n_A}{n_A + n_B} = 0.65$

we, therefore, have

$$n_B = \frac{n_A}{0.65} - n_A = n_A\left(\frac{1}{0.65} - 1\right) = \frac{(0.995\ \text{mol})(0.355)}{(0.65)} = 0.54\ \text{mol}$$

Problem-2. For the preceding problem, use the lever rule to obtain the amount of each compound in the vapour phase.

Soln. Now, we have

$$\frac{\text{Amount in the liquid phase}}{\text{Amount in the vapour phase}} = \frac{y_A - X_A}{X_A - x_A}$$

where X_A is the amount of fraction of ethylene bromide in the overall system. Substituting the values of x_A, y_A and X_A, we have

$$\frac{\text{Amount in the liquid phase}}{\text{Amount in the (liquid + vapour) phase}} = \frac{0.65 - (3/5)}{(3/5) - 0.57} = \frac{0.05}{0.02} = 2.25$$

Adding one on both sides and taking inverse, we get

$$\frac{\text{Amount in the vapour phase}}{\text{Amount in the (liquid + vapour) phase}} = \frac{1}{1 + 2.26}$$

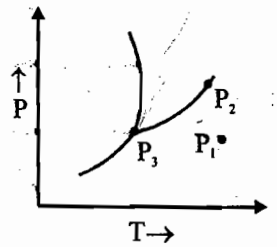
Amount in the vapour phase $= \frac{1}{(1+2.26)}(5\text{ mol})$

Therefore, $n_A = y_A\left(\frac{5\text{ mol}}{3.26}\right) = (0.65)\left(\frac{5\text{ mol}}{3.26}\right) = 0.996\text{ mol}$

$n_B = y_B\left(\frac{5\text{ mol}}{3.26}\right) = (0.3.50)\left(\frac{5\text{ mol}}{3.26}\right) = 0.0.54\text{ mol}$

PROBLEMS

1. The phase diagram of a pure substance is sketched below. The number of degree of freedom at points P_1, P_2 and P_3 are



(a) 21,0 (b) 1,2,0 (c) 2, 0, 1 (d) 0, 2, 1

Soln. At P_1

$P = 1 \quad C = 1$

$F = C - P + 2 = 1 - 1 + 2 = 2$

At P_2

Two phase in equation

$P=2,\ C = 1,\ F = 1$

At P_3

3 phase exist

$P = 3,\ C = 1,\ F = 0$

2. For the following system in equation, $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$

(a) 2, 2, 2 (b) 1, 3, 0 (c) 3, 3, 2 (d) 3, 2, 1

Soln. $CaCO_3 \rightleftharpoons CaO + CO_2$

(s) (s) (g)

Number of phases = 3

Number of component = 2 (because composition of all the phases can be expressed in term of CaO and CO_2)

$\therefore \quad F = C - P + 2 = 2 - 3 + 2$

$F = 1$

So, correct answer is (c)

3. The mathematical statement of Gibbs phase rule is

(a) $F = C - P + 2$ (b) $C = F - P + 2$ (c) $C = F - P + 1$ (d) $P = C + F + 2$

Soln. Correct answer is (a)

4. The number of phase in the system made of water and benzene are

(a) 1 (b) 2 (c) 3 (d) 0

Soln. $F = C - P + 2$

$P = F - C + 2 = 2-2+2$

$P = 2$

Correct answer is (b)

4. The maximum degrees of freedom in a one component system would be
(a) 2 (b) 3 (c) 4 (d) 5

Soln. $F = C + 2 - P = 1 + 2 - 1$
$F = 2$
Correct answer is (a)

5. The number of degrees of freedom in homogeneous liquid region of a two component system with a eutectic point, at one atmosphere pressure is
(a) 0 (b) 1 (c) 2 (d) 3

Soln. For two component, $F = 4 - P = 4 - 2 = 2$
Correct answer is (c)

PRACTICE SET

1. At the triplet point of water C, P, F are respectively
(a) 1, 3, 0 (b) 1, 3, 1 (c) 1, 2, 0 (d) 3, 3, 2

2. Which of the following equations predicts the lowering the melting point of ice with an increase of pressure?
(a) $\frac{dP}{dT}=\frac{(V_\ell - V_s)}{\Delta H_f}$ (b) $\frac{dP}{dT}=\frac{(V_\ell + V_s)}{\Delta H_f}$ (c) $\frac{dP}{dT}=\frac{T(V_\ell + V_s)}{\Delta H_f}$ (d) $\frac{dP}{dT}=\frac{T(V_\ell - V_s)}{\Delta H_f}$

3. Clausiu-Clapeyron equation is derived from
(a) First low of thermodynamics (b) Second low of thermodynamics
(c) Distribution law (d) None of these

4. There are many physical or chemical reactions which are accompanied by the appearance or disappearance of phase. These are known as
(a) Displacement reactions (b) Decomposition reactions
(c) Phase reactions (d) Thermal reaction

5. The lowest temperatures attainable with a freezing mixture is
(a) critical solution temperature (b) Eutectic temperature
(c) Triplet point (d) Critical temperature

6. What is the degree of freedom of a system having rated in equilibrium water vapour?
(a) 3 (b) 2 (c) 1 (d) 0

7. The minimum number of phases existing in a system would be
(a) 0 (b) 1 (c) 2 (d) 3

8. For the equilibrium, $Fe(s)+H_2O(g)\rightleftharpoons FeO(s)+H_2(g)$
What are the number of components, phases and degrees of freedom respectively?
(a) 3, 2, 3 (b) 2, 3, 3 (c) 3, 3, 2 (d) 2, 2, 3

9. Which of the following statements is/are not correct?
1. The phase diagram of a substance shows the regions of pressure and temperature at which the various phases are kinetically stable.
2. The freezing point when the pressure is 1 bar is called standard freezing point.
3. The normal and standard freezing points are negligibly different for most of the cases.
Select the correct answer using the code given below
(a) 1 only (b) 2 and 3 (c) 1 and 3 (d) 2 only.

10. What will be the number of phases, components and degrees of freedom respectively of the azeotropic mixture of water and ethanol at 10 atm at equilibrium?
(a) 2, 2 and 2 (b) 1, 2 and 3 (c) 2, 2 and 0 (d) 2, 3 and 1

11. Solid carbon reacts with oxygen in presence of a catalyst to form the gaseous oxides CO and CO_2. What is the number of degrees of freedom (variance) for the system once equilibrium has been attained?
(a) 0 (b) 1 (c) 2 (d) 3.

12. Consider the following statements
1. For a one component system, the maximum number of phases that can exist in equilibrium is three.
2. A system can have negative degrees of freedom.
3. The number of phases in a system does not depend on the amounts of the various substances present at equilibrium.
Which of the statements given below above is/are correct?
(a) 1 and 3 (b) 1 only (c) 3 only (d) 2 and 3.

13. What are the number of components and the number of degrees of freedom in

$Fe_{(s)} + H_2O_{(g)} \rightleftharpoons FeO_{(s)} + H_{2(s)}$

respectively?

(a) 3, 2 (b) 4, 3 (c) 3, 1 (d) 4, 2

14. For a pure susbtance, the triple point in a phase diagram has

(a) One degree of freedom (b) Two degrees of freedom

(c) Three degrees of freedom (d) Zero degree of freedom.

15. Sulfur can exist in four phases. The possible number of triple point is

(a) 1 (b) 2 (c) 3 (d) 4

ANSWER KEY					
Questions	1	2	3	4	5
Option	(a)	(d)	(b)	(c)	(b)
Questions	6	7	8	9	10
Option	(a)	(b)	(c)	(a)	(c)
Questions	11	12	13	14	15
Option	(d)	(a)	(a)	(d)	(d)

Chapter 12

Solution & Colligative Properties

Introduction:

Solution: The Homogeneous mixture of two or more than two components are known as solution. Component present in largest quantity is known as solvent and component other than solvent is known as solute. Solution are of various kinds; gaseous solution, liquid solution, solid solution (alloys, amalgam etc.)

All the properties which depend upon the number of particles of solute irrespective of their nature relative to the total number of particles present in the solution. These properties are known as Colligative Properties. These are

(i) Relative lowering of vapour pressure
(ii) Depression of freezing point
(iii) Elevation in boiling point
(iv) Osmotic pressure

(i) Relative lowering of vapour pressure:

When a solute is added to the solution its vapour pressure get decreases due to decrease in interaction between solvent molecule this decrease in vapour pressure is known as lowering of vapour pressure and its relative decrease with initial vapour pressure is known as relative lowering of vapour pressure.

$$\text{Relative lowering of vapour pressure} = \frac{P^0 - P}{P^0}$$

where, P^0 = initial pressure

P = Pressure after adding solute

Relative lowering of vapour pressure is equal to more fraction of solute.

According to Raoult's law "Relative lowering of vapour pressure is directly proportional to mole fraction of solute".

$$P^0 - P \propto \frac{n_2}{n_1 + n_2}$$

$$P^0 - P = P^0 \frac{n_2}{n_1 + n_2}$$

or, $$\frac{P^0 - P}{P^0} = \frac{n_2}{n_1 + n_2}$$

where, n_1 = number of moles of solvent

n_2 = number of moles of solute

$$n = \frac{\text{weight}}{\text{molecular weight}}$$

$$\frac{P^0 - P}{P^0} = \frac{\frac{w_2}{m_2}}{\frac{w_1}{m_1} + \frac{w_2}{m_2}}$$

For every dilute solutions $n_1 >> n_2$

$$\frac{P^0 - P}{P^0} = \frac{n_2}{n_1} = \frac{\frac{w_2}{m_2}}{\frac{w_1}{m_2}} = \frac{w_2 m_1}{w_1 m_2} \quad \therefore \quad \boxed{1 \text{ atm} = 760 \text{ torr}}$$

(i) For ideal solution, $\Delta H_{mixing} = 0$; $\Delta V_{mixing} = 0$

eg. Benzene and Toluene, Ethyl Bromide and Ethyl iodide, n-Hexane and n-Heptane

(ii) Relative lowering of vapour pressure can be measured by **Ostwald and Walker's dynamics method.**

Problem-1. The vapour pressure of two liquids P and Q are 80 and 60 torr respectively. The total vapour of the solution obtained by mixing 3 moles of P and 2 moles of Q would be

Soln. $n_A = 3, n_B = 2, \; x_A = \frac{3}{5}, x_B = \frac{2}{5}$

$P_A^0 = 80$ torr and $P_B^0 = 60$ torr

Total vapour Pressure $= x_A P_A^0 + x_B P_B^0 = \frac{3}{5} \times 80 + \frac{2}{5} \times 60 = 48 + 24 = 72$ torr

Problem-2. Benzene and toluene form nearly ideal solution. At 20°C the vapour pressure of benzene is 75 torr and that of toluene is 22 torr. The partial vapour pressure of benzene at 20°C in a solution containing 78 gm of benzene and 46 gm of toluene is

(a) 50 torr (b) 25 torr (c) 37.5 torr (d) 53.5 torr

Soln. Given: $P_B^0 = 75$ torr $\quad P_T^0 = 22$ torr

$w_B = 78$ gm $\quad w_T = 46$ gm

$m_B = 78 \quad m_T = 92$

$n_B = \frac{78}{78} = 1 \quad n_T = \frac{46}{92} = 0.5$

The partial vapour pressure of benzene $= x_B P_B = \frac{n_B}{n_B + n_T} P_B^0 = \frac{1}{1+0.5} \times 75 = \frac{1}{1.5} \times 75 = 50$ torr.

So, correct option is **(a)**

Problem-3. At 80°C, the vapour pressure of pure liquid A and B are 520 and 1000 mm respectively. If a mixture o f A and B boils at 80°C and 1 atm pressure the amount of A in the mixture is

(a) 34 % mole (b) 48 % mole (c) 50% mole (d) 52 % mole

Soln. Vapour Pressure of A = 520 mm = P_A^0

Vapour Pressure of B = 1000 mm = P_B^0.

Vapour Pressure of mixture = 760 mm.

$$760 = x_A \, 520 + x_B 1000 \quad \ldots (1)$$

We know that $x_A + x_B = 1$ ... (2)

From equation (i) and (ii) we get

$760 = (1 - x_B) 520 + 1000 \, x_B \Rightarrow 760 = 520 - 520 x_B + 1000 x_B$

$240 = 480\, x_B \Rightarrow x_B = \frac{1}{2} \Rightarrow x_A = \frac{1}{2}$ i.e. 50% mole

So, correct option is (c).

(ii) Depression of Freezing Point:

On adding solute to the pure solvent the freezing point of solution decreases, this decrease in freezing point is known as depression of freezing point.

Depression of freezing-point $\propto$ molal concentration (m)

$$\Delta T_f \propto m \quad \text{or} \quad \boxed{\Delta T_f = k_f.m}$$

If n is the number of moles of solute and W, the weight in grams of the solvent,

$$m = \frac{n}{W} \times 1000 \text{ (moles of solute per 1000gm of the solvent)}$$

$$\therefore \quad \boxed{\Delta T_f = K_f \times \frac{n}{w} \times 1000}$$

K_f is the molal depression constant or cryoscopic constant of the solvent, which is defined as the depression in freezing point produced when 1 mole of the solute is dissolved in 1000g of the solvent.

K_f may also be calculated from the following equation,

$$\boxed{K_f = \frac{RT^2}{1000 \ell_f}}$$

where T is the freezing point of the solvent and l_f is the latent heat of fusion per gram of solvent.

- Boiling point of a liquid increases with increase in external pressure. Therefore pressure cooker reduces the cooking time because boiling point of water inside a cooker is higher than the normal boiling point.
- Elevation in boiling point can be determined by

(a) Landberger's method. (b) Cottrell's method.

- $K_b = \frac{R\left(T_b^0\right)^2}{\ell_v\, 1000} = \frac{R\left(T_b^0\right) M_1}{\Delta H_{vap.} 1000}$

(iii) Elevation in boiling point:

On adding solute to the pure solvent boiling point of solution gets increases, this increase in boiling point is known as elevation in boiling point.

Elevation in boiling piont $\propto$ molal concentration

$$\Delta T_b \propto m$$

K_b is known as the molal elevation constant of the solvent or boiling point constant and

$$\boxed{K_b = \frac{RT^2}{1000\, \ell_v}}$$

Problem-4. K_f for water is 1.86°C m^{-1}. What is the molality of a solution which freezes at –0.192°C? Assuming no change in the solute by raising the temperature, at what temperature will solution boil? (K_b for H_2O = 0.515°C)

Soln. $\text{Molality} = \frac{\Delta T_f}{K_f} = \frac{0.192}{1.86} = 0.103\text{m}$

Again, $\Delta T_b = K_b.m = 0.515 \times 0.103 = 0.0532°C$

Assuming the boiling point of pure water to be 100°C the boiling point of the solution will be 100.0532°C.

Problem-5. A solution containing 2.44 gm of a solute dissolved in 75 gms of H_2O, boiled at 100.413 °C. Calculate the molar mass of the solute. K_b for $H_2O = 0.52$ K Kg/mole.

Soln. $W_1 = 75$ gms, $W_2 = 2.44$ gm, $K_b = 0.52$ K Kg / mole

$\Delta T_b = 100.413 - 100 = 0.413K$

$$\Delta T_b = \frac{1000\, K_b W_2}{W_1 M_2} \Rightarrow 0.413 = \frac{1000 \times 0.52 \times 2.44}{75 \times M_2}$$

$$M_2 = \frac{520 \times 2.44}{75 \times 0.413} = 40.96 \Rightarrow M_2 \simeq 41$$

Problem-6. 5% aquous solution by mass of a non-volatile solute boils at 100.15°C. Calculate the molar mass of the solute. $K_b = 0.52$ K kg / mole

(a) 821.7 gm/mole (b) 182.7 gm/mole (c) 287.3 gm/mole (d) 92.3 gm/mole

Soln. $\Delta T_b = 0.15$ K $K_b = 0.52$ K Kg / mole

5% aquous solution by mass means if the solution is 100 gm then there will be 5 gm of solute and 95 gm of solvent.

$W_2 = 5$ gm, $W_1 = 95$ gm

$$0.15 = \frac{1000 \times 0.52 \times 5}{M_2 \times 95}$$

$$M_2 = \frac{520 \times 5}{95 \times 0.15} = \frac{27.4}{0.15} = 182.66;\ M_2 = 182.7 \text{ gm/mole}$$

So, **correct option is (b).**

Problem-7. An aquous solution of non volatile solute boils at 100.17°C. At what temperature would it freeze?

Soln. $K_b = 0.52$ K Kg / mole and $K_f = 1.86$ K Kg/mole

$\Delta T_b = K_b \times m$

$$0.17 = 0.52\, m \Rightarrow m = \frac{0.17}{0.52}$$

$$\Delta T_f = K_f \times m = 1.86 \times \frac{0.17}{0.52} = .608 = 0.61$$

$\boxed{\Delta T_f = -0.61}$ negative due to depression.

(iv) Osmotic Pressure:

The external pressure which is applied to the solution side to prevent the process of osmosis is known as osmatic process, it can be represented by π. Osmotic pressure is directly proportional to concentration of solute.

$\pi \propto C$ and $\pi \propto T$

$\therefore$ $\pi \propto cT$

$$\pi = cRT \Rightarrow \pi = \frac{n}{V}RT \Rightarrow \pi V = nRT$$

$$\boxed{\pi V = \frac{w}{m}RT}$$

- The best semipermeable memebrane is that of Gelatinous precipitates of cupric ferrocyanide $Cu_2[Fe(CN)_6]$. This is prepared artificially by the reaction between $CuSO_4$ and $K_4[Fe(CN)_6]$.
- Depression in freezing point can be determined by

  (a) Beckmann's method (b) Rast's method.
- Ditillation of sea water is based on reverse Osmosis.
- When placed in hypotonic solutions, cells, swell and burst(haemolysis). On the other hand, when placed in hypertonic solutions, cells contract in size (plasmolysis). When excess of fertilizers like urea are applied, plasmolysis takes place. Hence, the plants dry up.
- Addition of HgI_2 to an aqueous solution of KI results in an increase in vapour pressure of solution because number of particles present in solution decreases.

  $2KI + HgI_2 \rightarrow K_2HgI_4 \rightarrow 2K^+ + HgI_4^{-2}$.
- Osmotic pressure is generally preferred for the determination of molecular masses of proteins.
- RBC when come in contact with 0.1% NaCl solution grow in size as water from salive water may enter them and they can ultimately burst.

Problem-8. A solution containing 8.6 gm per dm^3 of urea was found to be isotonic with a 5% solution of an organic non-volatile solute. Calculate the molar mass of the later.

Soln. 5% sol. = 5 gm 100 mL.

= 5 gm per 0.1 lit

$\pi_{urea} = \pi_{solution}$

$$\frac{W_1}{m_1 v_1}RT = \frac{W_2}{m_2 V_2}RT$$

$$\frac{8.6}{60\times1} = \frac{5}{m_2\times0.1} \Rightarrow m_2 = \frac{5\times60}{8.6\times0.1} = 348.33$$

Problem-9. At 37°C the osmotic pressure of blood is 7.65 atm. How much glucose should be used per litre for a intravenous injection.

Soln. M. wt of glucose = 180 and T = 37 + 273 = 310 K

$\pi = 7.65$ atm, $R = 0.0821$ lit atm/K – mole

$$\pi = \frac{w}{m}\frac{RT}{V} \Rightarrow 7.65 = \frac{w}{180}\times\frac{0.0821\times310}{1} \Rightarrow w = \frac{7.65\times180\times1}{0.0821\times310} = 54.10 \text{ gm}$$

Vant Hoff factor (i) :

$$i = \frac{\text{normal molar mass}}{\text{observed molar mass}}$$

Dissociation

$$\alpha = \frac{i-1}{n-1}$$

Association

$$\alpha = \frac{i-1}{\frac{1}{n}-1}$$

$BaCl_2 \longrightarrow Ba^{++} + 2Cl^-$ $\quad n = 3$

$K_4[Fe(CN)_6] \longrightarrow 4K^+ + [Fe(CN)_6]^{4-}$ $\quad n = 5$

Problem-10. Acetic acid associates in benzene to form double molecules. 1.65 gm of AcOH when dissolved in 100 gm of benzene raised the boiling point by 0.36°C. Calculate Van't Hoff factor and degree of association of AcOH in benzene.

(Given, $K_b = 0.52K - Kg/mole$)

$K_b = 0.52\ K - Kg/mole, W_2 = 1.65\ gm, \Delta T_b = 0.36k$

$W_1 = 100\ gm \quad M_2 = ?,\ i = ?,\ \alpha = ?$

$$\Delta T_b = \frac{1000\ K_b\ W_2}{W_1 M_2} = \frac{1000 \times 2.57 \times 1.65}{M_2 \times 100}$$

$$\Rightarrow \quad 0.36 = \frac{1000 \times 2.57 \times 1.65}{M_2 \times 100} \Rightarrow M_2 = \frac{10 \times 2.57 \times 1.65}{0.36} = 117.79$$

$$i = \frac{\text{normal molar mass}}{\text{observed molar mass}} \Rightarrow i = \frac{60}{117.79} = 0.51$$

$$\alpha = \frac{i-1}{\frac{1}{n}-1} \Rightarrow \alpha = \frac{0.51-1}{\frac{1}{2}-1} = \frac{-0.49}{-0.5} = 0.98$$

Problem-11. A 0.5% aq. solution of KCl was found to freeze at –0.24°C. Calculate van't Hoff factor and degree of dissociation of solute at this concentration.

$K_f = 1.86\ K - Kg/mole$

Soln. $K_f = 1.86\ K - Kg/mole \qquad \Delta T_f = 0 - (-0.24) = 0.24\ K$

$W_2 = 5\ gm, W_1 = 100\ gm, M_2 = ?, i = ?, \alpha = ?$

$$\Delta T_f = \frac{1000\ K_f W_2}{M_2 W_1} \Rightarrow 0.24 = \frac{1000 \times 1.86 \times 5}{M_2 \times 100}$$

$$M_2 = \frac{1000 \times 1.86 \times 5}{100 \times 0.24} = 38.94$$

$$i = \frac{74.5}{38.94} = 01.92$$

$$\alpha = \frac{1.92-1}{2-1} = 0.92 \text{ or } 92\%$$

Problem-12. Freezing point depression of a $\frac{1}{200}$ molal solution of Na_2SO_4 in H_2O was found to be 0.0265°C. Calculate degree of dissociation of salt at this concentration. $K_f = 1.86\ K - Kg/mole$.

Soln. $K_f = 1.86\ K - kg/mole \qquad \Delta T_f = 0.0265\ K \qquad n = 3$

$W_2 = \frac{1}{200} \times 142\ gm$ in $W_1 = 1000\ gm$

$$\Delta T_f = \frac{1000\ K_f\ W_2}{M_2 W_1}$$

$$0.0265 = \frac{1000 \times 1.86 \times \frac{1}{200} \times 142}{M_2 \times 1000}$$

$$M_2 = \frac{1.86 \times 142}{200 \times 0.026} = 49.83$$

$$i = \frac{142}{49.83} = 2.85$$

$$\alpha = \frac{2.85 - 1}{3 - 1} = \frac{1.85}{2} = 0.925 = 0.925 \quad \text{or} \quad 92.5\%$$

Problem-13. Which of the following salt has the same value of van't Hoff factor as that of $K_3\left[Fe(CN)_6\right]$.

(a) $Al_2(SO_4)_3$ (b) NaCl (c) Na_2SO_4 (d) $Al(NO_3)_3$.

Soln. **(d)**

Problem-14. Van't Hoff factor for $AlCl_3$ is:

(a) 3 (b) 4 (c) 1/3 (d) 1/2.

Soln. **(d)**

Problem-15. 75.2 gm of phenol is dissolved in 1 Kg of solvent ($K_f = 14$). The depression in freezing point is 7K. Find the percentage of phenol that dimerises

(a) 75 (b) 25 (c) 65 (d) 35

Soln. $\Delta T_f = \frac{1000\, K_f\, W_2}{M_2\, W_1} \Rightarrow 7 = \frac{1000 \times 14 \times 75.2}{M_2 \times 1000}$

$$M_2 = \frac{1000 \times 14 \times 75.2}{1000 \times 7} = 150.4$$

$$i = \frac{94}{150.4} = 0.625$$

$$\alpha = \frac{0.625 - 1}{\frac{1}{2} - 1} = \frac{0.375}{\frac{1}{2}} = 0.75 \text{ i.e. } 75\%$$

So, correct option is (a).

Problem-16. What is molarity of H_2SO_4 solution that has a density 1.84 gm/cc at 35°C and contain 98% by weight.

(a) 4.18 molar (b) 8.14 M (c) 18.14 M (d) 18.40 M

Soln. $d = 1.84$ gm/cc, $V = \frac{M}{d} = \frac{98}{1.84}$

$W = 98$ gm $\quad V = 100$ mL

$$\text{Molarity} = \frac{1000W}{MV} = \frac{1000 \times 98}{\frac{98}{1.84} \times 100} = 18.40$$

So, correct option is (d)

Problem-17. Equal volumes of 10^{-4} molar $CaCl_2$ and 3×10^{-5} molar NaF solution are mixed with a ppt of CaF_2 occur.

Soln. $K_{sp} = 1 \times 10^{-11}$ for CaF_2

10^{-4} M $CaCl_2$ $\quad 3 \times 10^{-5}$ NaF

$CaCl_2 \longrightarrow Ca^{++} + 2Cl^-$

$10^{-4}M \quad 10^{-4}M \quad 2\times10^{-4}M$

$NaF \longrightarrow Na^+ + F^-$

$3\times10^{-5} \quad 3\times10^{-5} \quad 3\times10^{-5}$

$CaF_2 \longrightarrow Ca^{++} + 2F^-$

$$\text{Ionic product} = \left[Ca^{++}\right]\left[F^-\right]^2 = \left[10^{-4}\right]\left[2\times3\times10^{-5}\right]^2 = 10^{-4}\times36\times10^{-10} = 36\times10^{-14}$$

K_{sp} > Ionic product so no ppt.

Problem-18. 250 mL of 0.01 M K_2SO_4 is mixed with 250 mL of 0.2 molar KCl solution. What is the concentration of K^+ ions in the resulting solution.

(a) 0.1 Mr (b) 0.2 Mr (c) 0.3 Mr (d) 0.4 Mr

Soln. 250 mL

$K_2SO_4 \longrightarrow 2K^+ + SO_4^{2-}$

0.10M $\quad 2\times0.10$ M $\quad$ 0.10 M

250 mL

$KCl \longrightarrow K^+ + Cl^-$

0.2 M $\quad$ 0.2M $\quad$ 0.2 M

$$M_1V_1 + M_2V_2 = M_3V_3$$

$$2\times0.10\times250 + 0.2\times250 = M_3(250+250) \Rightarrow 250\times0.4 = M_3\times500$$

$$M_3 = \frac{0.4}{2} = 0.2$$

So, correct option is (b)

Molarity:

Molarity = number of moles of solute present in per **litre** of solution

$$\text{Molarity} = \frac{\text{no. of moles of solute}}{\text{volume of solution (lit)}} = \frac{\frac{\text{wt}}{\text{mol.wt}}}{\frac{\text{v}}{100}} = \frac{1000W}{MV}$$

$$\boxed{M_1V_1 + M_2V_2 = M_3(V_1+V_2)}$$

$$d = M\left[\frac{1}{m} + \frac{M'}{1000}\right]$$

where, M → Molality, m → molarity, M' → molecular mass

Problem-19. The density of 3.60M H_2SO_4 i.e 29% of H_2SO_4 by mass will be

(a) 1.88 (b) 1.22 (c) 1.45 (d) 1.64

Soln. Molarity = 3.6 W = 29 gm $\quad V = \frac{\text{Mass}}{\text{density}} = \frac{100}{d}$

$$\text{Molarity} = \frac{1000W}{MV} = \frac{1000W}{M \times \frac{\text{Mass}}{d}} = \frac{1000\,Wd}{M \times \text{Mass}}$$

$$3.6 = \frac{1000 \times 29 \times d}{98 \times 100} \Rightarrow d = \frac{3.6 \times 98 \times 100}{1000 \times 29} \Rightarrow d = 1.22$$

So, Correct answer is (b)

Molality (m): Molality = number of moles of solute present per kg of solvent.

$$m = \frac{\text{number of moles of solute}}{\text{mass of solvent}} = \frac{\frac{wt}{\text{mol.wt.}}}{\text{wt. of solvent in } \frac{gm}{1000}} = \frac{wt \times 1000}{\text{M.wt} \times \text{wt of solvent}}$$

$$\Rightarrow \boxed{m = \frac{W \times 1000}{M\,W_2}} \qquad \left[\text{Mole fraction of component} = \frac{\text{Number of moles of component}}{\text{Total number of mole of component}}\right]$$

Problem-20. If the molality (m) of an aq. solution of cane sugar ($C_{12}H_{22}O_{11}$) is 0.45. What is the mole fraction of cane sugar in solution.

(a) 0.008 (b) 0.08 (c) 0.016 (d) 0.018

Soln. $m = 0.45$ $W_1 = ?$ $M = 342$ $W_2 = 1000$ gm

0.45 gm in 1000 gm of solvent.

$$0.45 = \frac{wt \times 1000}{342 \times 1000};\ wt = 0.45 \times 342 = 153.9 \simeq 154$$

$$\text{Number of moles} = \frac{153.9}{342} = 0.45 \quad (\text{for cane sugar})$$

$$\text{for solvent number of moles} = \frac{1000}{18} = 55.55$$

$$\text{mole fraction of solute} = \frac{0.45}{0.45 + 55.55} = \frac{0.45}{56} = 0.008$$

So, correct answer is (a)

Problem-21. The mole fraction of solute in one molal aq. solution is

(a) 0.027 (b) 0.036 (c) 0.018 (d) 0.009

$$x = \frac{1}{55.55 + 1} = \frac{1}{56.55} = 0.0176 \simeq 0.018$$

So, correct answer is (c)

Henry law: This law gives a quantitative relation between pressure and solubility of gas.

It is only applicable if gas is not largely soluble in the solution, even through saturated, may be very dilute.

It states, at contant temperature the solubility of gas in a liquid is directly proportional to the partial pressure of gas present above surface of solution.

solubility $\propto p$

solubility $= K_H P$, where, K_H = Henry constant

OR

"The concentration is proportional to the mole fraction of the dissolved substance".

So, $x \propto C$

$x = K_H C$ where, x = mole fraction and C = concentration.

In terms of mole fraction mole fraction of gas is directly proportional to the partial fraction of gas.

$P = K_H x$

Higher the value of K_H, lower will be the solubility of gas.

Problem-22. Henry law constant of methyl bromide is 0.159 moles/lit atm at 25°C. What is the solubility (in moles/lit) of CH_3Br in water at 25°C and partial pressure of 125 mm Hg.

Soln. $p = 125 \text{ mm of Hg} = \frac{125}{760} = \text{atm}$

$s = K_p = 0.159 \times \frac{125}{760} = 0.026 \text{ mole / lit}$

Non-Ideal solution (Deviation from Raoult's law)

Positive deviation	Negative deviation
ΔS= +ve	ΔS= +ve
ΔV= +ve	ΔV= –ve
ΔH= +ve(endothermic)	ΔH= –ve(exothermic)

Problem-23. The complex compound $K_4\left[Fe(CN)_6\right]$ is 45% dissociated in 0.1 M aqueous solution of complex at 27°C. What will be the osmotic pressure of the solution?

Soln. $\alpha = 0.45, T = 27 + 273 = 300K,\ R = 0.0821$

$0.45 = \frac{i-1}{5-1} \Rightarrow i = 2.80$

0.1M means that 100mL is 1000 mL

$\pi V = mRT$

$\pi = \frac{2.80 \times 0.0821 \times 300 \times 100}{1000} = 6.896 \text{ atm}$

Problem-24. Ethylene glycol is a colourless liquid used as automobile antifreeze. If the density at 20°C of a 4.028 m solution of ethylene glycol in H_2O is 1.0241 gm/mL. What is the molarity of soln (molar mass of ethylene glycol = 62.07 gm/mole).

Soln. 4.028 m = 4.028 mole in 1000 gm of H_2O

$d = \frac{m}{v} \Rightarrow v = \frac{M}{d} = \frac{62.07}{1.0241} = 60.61 \text{ mL}$

$M = \frac{1000\ W}{M\ V}$

$d = \left[\frac{1}{m} + \frac{M'}{100}\right] M$

$1.0241 = \left[\frac{1}{4.028} + \frac{62.07}{1000}\right] M$

$1.024 = [0.24 + 0.06] M \Rightarrow 1.024 = 0.310M$

$M = \frac{1.024}{0.310} = 3.33$

PRACTICE SET

1. According to Roults law the relative lowering of vapour pressure of a solution of a non- volatile non-electrolyte is equal to
   (a) mole fraction of solvent (b) weight percent of solute
   (c) mole fraction of solute (d) weight percent of solvent

2. The freezing point of 0.2 molal solution of non-volatile solute in benzene is 1.02^0 lower than the freezing point of pure benzene. The molar depression constant of benzene is:
   (a) 2.04 (b) 5.1
   (c) 1.86 (d) 0.102

3. A pressure cooker reduces the cooking time because:
   (a) The heating is more uniform (b) the higher pressure tendierizes the food.
   (c) The vapour pressure of water is increased (d) the boiling point of water is elevated

4. The best method for determination of molecular weight of a non-volatile non-electrolyte is:
   (a) Hoffman's method (b) Victor Mayer's method
   (c) Cryoscopic method (d) Density measurement

5. Ideal solution follows Roult's Law at:
   (a) low temperature and high concentration (b) high temperature and low concentration
   (c) low temperature and low concentration (d) all temperature and all concentration

6. For ideal solution:
   (a) $\Delta V_{mix} > 0, \Delta H > 0$ (b) $\Delta V_{mix} < 0, \Delta H_{mix} < 0$
   (c) $\Delta V_{mix} = 0, \Delta H_{mix} = 0$ (d) $\Delta V_{mix} < 0, \Delta H_{mix} > 0$

7. An ideal solution is formed by mixing two pure liquids. For this solution
   1. $\Delta H_{mix} = 0$ 2. $\Delta V_{mix} = 0$ 3. $\Delta G_{mix} = 0$ 4. $\Delta S_{mix} = 0$
   (a) Only 1 is true (b) Only 1 and 2 are true
   (c) Only 2 and c are true (d) All are true.

8. The osmotic pressure (in atm) of 0.1 M NaCl solution at the room temperature is:
   (a) 2.5 (b) 5.0 (c) 7.5 (d) 10

9. Ethanol and methanol form ideal solutions and their vapour pressures in the pure form are 44.5 torr and 88.7 torr at 295 K, respectively. Their partial pressures (in torr) in a solution obtained by mixing 50 gms of each, are, respectively
   (a) 18.3 and 52.3 (b) 52.3 and 18.3 (c) 36.5 and 26..3 (d) 26.3 and 36.5

10. The osmotic pressure of blood is 7.4 atm at 27°C. The number of moles of glucose (per litre) that should be used for an intravenous injection so that it has the same osmotic pressure as that of blood is:
    (a) 0.1 (b) 0.2 (c) 0.3 (d) 0.4

11. The magnitude of the colligative property of a two-component solution depends on the
    (a) Number of solute molecules (b) Number of solvent molecule
    (c) Number of solute molecules relative to that of solvent molecules.
    (d) Total number of solvent and solute molecules.

12. The vapour pressure of crystalline zirconium chloride follows the equation log p (in mm) = –5400/T + 11.766. The heat of sublimation (in kcal mol^{-1}) at 437°C is:
    (a) 24700 (b) 24.7 (c) 103.2 (d) 4.7

13. 5.0 gm of a non-dissociating organic substance dissolves in 100 g of water to generate an osmotic pressure of 7.15 atm at 25°C. The molar mass of the substance is:

$(R = 0.08206 \text{ atm L mol}^{-1} \text{ K}^{-1})$

(a) 171 g mol^{-1} (b) 342 g mol^{-1} (c) 684 g mol^{-1} (d) 35640 g mol^{-1}

14. The vapour pressure of a solvent decresed by 5 mm of Hg, when a non-volatile solute was added to the solvent. The mole fraction of the solute in the solution is 0.2. What would be the mole fraction of the solvent, if decrease in the vapour pressure is to be 15 mm of Hg?

(a) 0.8 (b) 0.6 (c) 0.4 (d) 0.2

15. 1.2 g of acetic acid when dissolved in 100 g of benzene raised the boiling of benzene by 0.26°. What is the value of van't Hoff's factor of acetic acid in benzene?
(Molal elevation constant of benzene is 2.58°)

(a) 2 (b) 1 (c) 5 (d) 0.5

ANSWER KEY					
Questions	1	2	3	4	5
Option	(c)	(b)	(b)	(c)	(d)
Questions	6	7	8	9	10
Option	(c)	(b)	(b)	(a)	(c)
Questions	11	12	13	14	15
Option	(a)	(b)	(a)	(c)	(d)